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Haloacetic Acid Formation During Chloramination: Role of Environmental Conditions, Kinetics, and Haloamine Chemistry

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Haloacetic Acid Formation During Chloramination: Role of Environmental Conditions, Kinetics, and Haloamine Chemistry

by

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Dissertation

Presented to the Faculty of the Graduate School of

The University of Texas at Austin

in Partial Fulfillment

of the Requirements

for the Degree of

Doctor of Philosophy

The University of Texas at Austin

December, 2006

Dedication

Dedicated to my parents

Phillip E. Pope

And

Judy H. Pope

Acknowledgements

I would first like to thank my supervising professor Dr. Gerald E. Speitel Jr. His guidance and patience always helped me through any problems I encountered. He has been an excellent mentor and I greatly value the opportunity I had to work with him. I would also like to think my dissertation committee for their guidance and wisdom. I consider myself fortunate to have had the opportunity to learn from them both inside and outside of classroom.

In the six years I spent studying at UT, I not only found a wonderful home in Austin, but have made many friends in EWRE. I thank the research groups of Dr. Speitel, Dr. Lawler, Dr. Katz, and Dr. Collins for all the help they have provided; but, I especially thank Julian, Dave, Jeff, Ram, and the rest of the gang on the 9th floor for all the fruitful discussions and fun over the years.

I gratefully thank my parents for instilling in me the value of education and the confidence that I could succeed with hard work. I also thank my brother for just being my brother, reminding me not to forget to have fun. Most importantly, I not only received my doctorate from this institution, but also found the love of my life. Kristen, your support and patience with me was remarkable, especially during this last push.

Greg Pope
August 26, 2006

Haloacetic Acid Formation During Chloramination:
Role of Environmental Conditions, Kinetics, and Haloamine Chemistry

Publication No._____

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The University of Texas at Austin, 2006

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This dissertation addresses the development of strategies to limit haloacetic acid (HAA) formation resulting from chloramination in drinking water treatment. The impact of several variables that influence HAA formation, such as natural organic matter (NOM), pH, Cl_2:N ratio, disinfectant residual concentration, and bromide ion concentration were studied. A multi-factor, two-level, factorial experimental design and statistical analysis of the collected data determined pH and bromide concentration to be the most significant factors contributing to HAA formation. In addition to these variables, the rate of HAA formation during chloramination is a key consideration in determining strategies for minimizing formation. The kinetics of HAA formation during chloramination are characterized by an initial rapid period of formation followed by a period of slower formation. However, many plants now have a significant period of free chlorination prior to ammonia addition for purposes of meeting disinfection requirements. During short periods of prechlorination (5 or 20 minutes), significantly more HAA formation occurred relative to chloramination alone. This research was not

only focused on explaining DXAA formation in terms of NOM characteristics and basic water quality and operating parameters, but also expands upon our knowledge of haloamine chemistry with a particular focus on DBP formation. In the presence of bromide, bromine-substituted haloacetic acids, as well as bromine-substituted haloamines, are formed, greatly increasing the number of chemical species that may be relevant in controlling DXAA formation. These bromine-substituted haloamines decay more rapidly and are significantly more reactive than their chlorine-substituted counterparts in forming HAAs. This research provides the fundamental underpinning for new strategies that will help water utilities select operating conditions that minimize the formation of the most reactive haloamine species, thereby leading to decreased HAA formation during chloramination.

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CHAPTER 1: Introduction

1.1. BACKGROUND

Drinking water must be disinfected prior to human consumption to inactivate pathogenic microorganisms. Chlorine has been used for disinfection for many years; however, carcinogenic and mutagenic disinfection by-products (DBPs) form as a result of chlorine reacting with naturally present organic material in the water. As a result, alternative disinfection processes have been sought to limit DBP production while still providing adequate disinfection. Chemicals such as ozone, chloramines, and chlorine dioxide have been used in place of chlorine; in particular, interest in chloramines is growing because of attractive economics and lower DBP formation than chlorine.

Though chloramines, which are produced when chlorine and ammonia are mixed in aqueous solution, limit many DBPs of regulatory concern, significant concentrations of dihaloacetic acids (DXAAs) can still be formed. The chloramines include monochloramine, dichloramine, and trichloramine. Of these, monochloramine is the species that dominates under normal drinking water treatment conditions. In the presence of bromide, bromine-substituted haloacetic acids, as well as bromine-substituted haloamines, are formed, greatly increasing the number of chemical species that may be relevant in controlling DXAA formation. Limiting the formation of bromine-substituted HAAs is of particular interest because recent studies have shown that they may pose a greater health risk than their chlorine-substituted counterparts (Bull *et al*., 1995; Karagalioglu *et al*., 2000; Karagalioglu *et al.,* 2002).

Recently, many utilities have begun to use chloramines as a secondary disinfectant in response to current and anticipated DBP regulations; thus, many plants now have a significant period of free chlorination prior to ammonia addition for purposes

of meeting CT requirements (Seidel *et al.,* 2000; Connell *et al.,* 2000). This pre-chlorination prior to ammonia addition necessitated by disinfection regulations is a great concern with respect to DBP formation. Clearly, significant exposure to free chlorine will produce more DBP formation than with chloramines alone, and pre-chlorination is likely to affect both the rate and extent of DBP formation during subsequent chloramination. Many utilities now face a chlorine/chloramines/CT balancing act that will only get more difficult in the future. In many respects, the rate of DBP formation during chloramination is the key issue (*i.e.*, how much additional DBP formation will occur in the treatment plant and distribution system after free chlorination is terminated by ammonia addition?). Therefore, the better understanding of DXAA formation kinetics with chloramines provided by this research is an important input to the complicated decision-making process facing some utilities.

This research proposes that the variability in DXAA formation and speciation is associated with the relative concentrations of the different haloamine species and their varying reactivities. Therefore, a better understanding of haloamine speciation in the presence of bromide under the range of conditions encountered in drinking water treatment, as well as the reactivity of the various haloamine species in forming DXAA, will allow development of new approaches for minimizing DXAA formation.

1.2. RESEARCH OBJECTIVES

The overall objective of this research was to increase our understanding of DXAA formation during chloramination and the factors that influence it, with particular emphasis on the role of bromide. Previous work indicates that pH, chlorine-to-ammonia-nitrogen (Cl_2/N) ratio, bromide concentration, temperature, precursor type and concentration, chloramine residual concentration, and mode of chloramine addition affect

the formation of HAAs. The overall research objective was achieved by focusing on the following issues:

1. A better understanding of the effects of treatment processes on both the removal and reactivity of natural organic matter (NOM) fractions. with respect to DXAA formation.
2. A better delineation of the influence of pH, Cl_2/N ratio, temperature, and bromide concentration on DXAA formation.
3. Characterization of DXAA formation kinetics and the impact of treatment processes on the kinetics, in particular the impact of significant periods of prechlorination.
4. Characterization of the reactivity of the various haloamine species in forming DXAA.
5. A better definition of haloamine speciation in the presence of bromide under the range of conditions encountered in drinking water treatment.

To address the above issues, this research consisted of laboratory experimentation, mathematical modeling, and sampling of a typical treatment plant and distribution system. A series of batch screening experiments identified the relative significance of the many variables that could affect DXAA formation during chloramination. DXAA formation kinetics were studied in several different waters, including the effects of treatment (*i.e.*, coagulation or softening), bromide concentration, water temperature, and prechlorination. The laboratory kinetic measurements were confirmed by sampling a full-scale treatment plant and distribution system. The reactivity of haloamine species were studied by isolating the individual haloamines to the extent possible, then reacting them with natural waters. The haloamine reactivity experiments were supported by a series of haloamine speciation experiments, which were

conducted over the range of pH and alkalinity typical of natural waters. Current analytical techniques can only accurately measure haloamines at high concentrations, or cannot distinguish among them, measuring total oxidant concentrations. Therefore, a key to this research was the ability to measure the concentrations of the individual haloamine species at concentrations typical of drinking water treatment through the application of a novel analytical technique, membrane introduction mass spectrometry (MIMS). The insight into haloamine chemistry gained by MIMS allowed a mathematical model to be developed to assist in conceptualizing the complex chemistry and in interpreting experimental data.

This research sought to provide the fundamental underpinning for new strategies that will help engineers and treatment plant operators select operating conditions that minimize the formation of the most reactive haloamine species, thereby leading to decreased DXAA formation during chloramination. Although the emphasis of this research was on DXAA formation, the improved understanding of haloamine chemistry and reactivity that also was gained may provide a new basis for better understanding the formation of other DBPs formed by haloamines. Clearly, the use of chloramination will continue to grow in the future and almost certainly DBPs in addition to DXAA will become of concern.

CHAPTER 2: Literature Review

2.1. INTRODUCTION

Two AWWARF-sponsored projects, initiated in the mid-1990's, identified two previously unknown issues with respect to chloramination: (1) dihalogenated haloacetic acids (DXAAs) are by far the most commonly formed haloacetic acids (HAAs) (Symons *et al*., 1998; Singer *et al*., 1999), which is in contrast to chlorination where significant formation of both di- and trihaloacetic acids is commonplace, and (2) because chloramination does not limit the formation of DXAAs as well as it does other disinfection by-products (DBPs), some utilities may have difficulty meeting the Stage 2 DBP rule for the five regulated haloacetic acids (HAA5). Under this rule, systems must conduct an evaluation of their distribution systems to identify the locations with high DBP concentrations. These locations will then be used by the systems as the sampling sites for compliance monitoring. Compliance with the maximum contaminant level (MCL) of 60 μg/L for HAA5 will be calculated for each monitoring location in the distribution system as the locational running annual average (LRAA). This approach differs from current requirements, which determine compliance by calculating the running annual average of samples from all monitoring locations across the system. DBPs of regulatory concern, other than DXAAs, are well-controlled by chloramination; therefore, a better understanding of DXAA formation and control is the primary research need to help ensure that all utilities are able to use chloramination in the future, should they so desire.

In setting the stage for this research, it is useful to first reiterate the relative merits of chloramination over chlorination. Even though some problems with DXAA may be encountered, chloramination is vastly superior to chlorination with respect to HAA

formation (Speitel, 1999), as shown by the data in Table 2-1. Typically, HAA formation with concurrent addition of chlorine and ammonia is 5 to 20% of that observed with chlorination. Even DXAA formation in chloramination tends to be less than that observed in chlorination. For example, Zhang *et al*. (1999), working with Suwannee River fulvic acid, observed that DXAA formation after 5 days of contact with chloramines was 40 to 50% of that with chlorine. Singer *et al*. (1999) found that DXAA formation after 24 hours of contact with chloramines was 10 to 30% of that with chlorine in four waters that were alum coagulated, settled, and filtered prior to disinfectant addition. The potential DXAA problems in chloramination are generally small enough to reasonably expect that an improved understanding of DXAA formation will permit utilities to meet the Stage 2 MCL through relatively minor changes in treatment practices.

Table 2-1 – Relative HAA formation with chloramination versus chlorination

Water Source	**Relative HAA Formation from Chloramination***	**Reference**
Seymour Reservoir (BC)	23% of HAASDS†	Long *et al*. (1992)
Capilano Reservoir (BC)	15% of HAASDS	Long *et al*. (1992)
Quabbin Reservoir (MA)	6 – 20% of HAASDS	Zhu and Reckhow (1993)
Mississippi River (LA)	10% of HAASDS	Lykins *et al*. (1994)
Palm Beach (FL) & Myrtle Beach (SC) extracts	5 – 10% of HAASDS	Cowman and Singer (1996)
Lake Austin (TX)	3 – 20% of HAAFP‡	Symons *et al*. (1998)
Lake Houston (TX)	7 – 17% of HAAFP	Symons *et al*. (1998)
CA State Project	5 – 30% HAAFP	Symons *et al*. (1998)
Suwannee River fulvic acid	26 – 29% HAAFP	Zhang *et al*. (1999)

* Chloramination HAA concentration/chlorination HAA concentration x 100

† Haloacetic acid simulated distribution system concentration with chlorine

‡ Haloacetic acid formation potential with chlorine

2.2. FACTORS INFLUENCING DXAA FORMATION

Many factors may influence DBP formation during chloramination. These include:

- pH
- Cl_2/N mass ratio
- Bromide concentration (influences both DBP and chloramine speciation)
- Temperature
- Precursor type and concentration
- Chloramine concentration
- Mode of chloramine addition (concurrent or staggered addition of chlorine and ammonia)
- Pretreatment by other oxidants, in particular ozone, prior to chloramine addition.

With respect to HAAs, the two AwwaRF-sponsored projects cited above, as well as a few pilot and full-scale studies, largely provide the current basis for our understanding of HAA formation during chloramination. In this section, the available information is evaluated in the context of the factors influencing DBP formation, listed above.

To briefly summarize the past AwwaRF projects, Symons *et al*. (1998) performed detailed batch studies on three natural waters looking at pH (6, 8, 10), Cl_2/N mass ratio (3, 5, and 7/1), residual chloramine concentration (1, 2, and 4 mg/L as Cl_2), bromide concentration (ambient and ambient plus 0.5 mg/L), mixing intensity during chlorine and ammonia addition (low, medium, high), and delayed ammonia addition (30 sec). The work also included pilot plant runs on three waters, distribution system sampling and limited batch studies on an additional five waters, and analysis of historical data for the

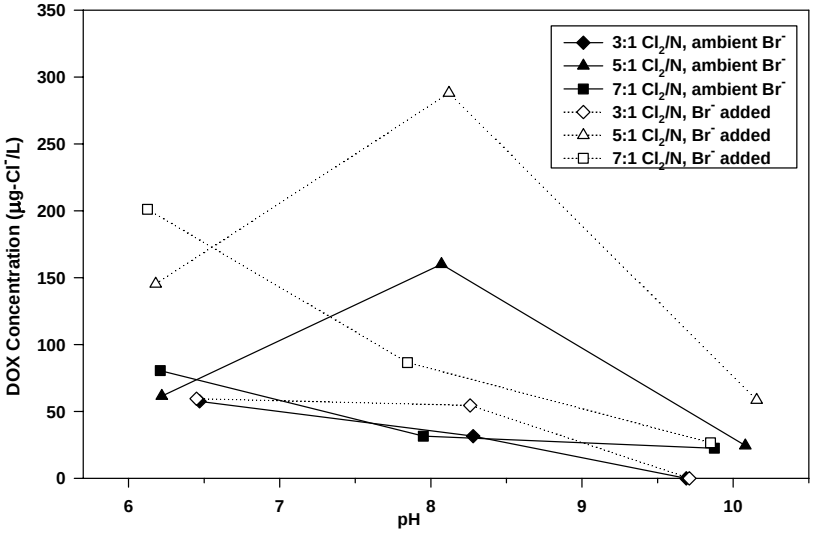
five waters. The primary analytical measurements were dissolved organic halogen (DOX) and trihalomethanes (THMs). HAA and cyanogen halide (CNX) concentrations were measured on a subset of the experiments run. The primary limitations of this study are the absence of a comprehensive HAA data set (because the significance of HAA formation was unknown entering the project and did not become apparent until well into the project), a focus almost solely on natural waters to consider worst case situations (*i.e*., the effect of treatment was largely, but not totally, ignored), and detailed characterization of the natural organic matter (NOM) was not performed.

Singer *et al*. (1999) examined the effect of ozonation on chlorine and chloramine DBP formation, including HAAs, in a series of batch experiments. Because the project included ozonation, chlorination, and chloramination, the range of chloramination conditions had to be limited for practical considerations and included one pH (8) and one Cl_2/N mass ratio (4/1). Both source water and treated water (various combinations of ozonation and coagulation, settling, and filtration) were studied for five waters of varying characteristics, especially in terms of the nature of the NOM. Most experiments, however, were performed on model waters prepared from hydrophobic extracts of the five water sources. The model water experiments examined the effects of ozonation pH and total organic carbon (TOC), inorganic carbon, and bromide concentrations on DBP formation. Also, much more characterization of NOM was performed than on the Symons *et al*. project, and the utility of such measurements in providing information on reactivity and the potential for DBP formation was demonstrated. With respect to HAA formation in chloramination, the work of Singer *et al*. (1999) is limited by the single pH and Cl_2/N values studied and by the uncertainty associated with extrapolating results from hydrophobic extracts to natural waters. A more detailed evaluation of the two

AwwaRF-sponsored projects and other relevant research is provided below for the factors that influence DBP formation during chloramination.

2.2.1. pH and Cl_2/N Ratio

Batch studies by Symons *et al*. (1998) showed that, in general, DBPs (including HAAs) decreased in concentration as the pH increased and the Cl_2/N ratio decreased. For example, at a Cl_2/N mass ratio of 3/1 the HAA_6 concentration at pH 10 was typically 30 to 50% of that at pH 6. Some significant departures from the general trend were noted, however, around neutral pH (7-8). For example, the DOX data for Lake Austin water (Figure 2-1) showed significant concentration peaks around pH 8 for a Cl_2/N mass ratio of 5/1, both at the ambient bromide concentration and with 0.5 mg/L of bromide added. These results suggest either a pH dependence of NOM reactivity or a pH dependence of haloamine speciation (and thereby reactivity). The former is more likely near neutral pH; for example, the reaction rates for chlorination of various phenols peak in the vicinity of pH 8 (Stumm and Morgan, 1996). Unfortunately, insufficient HAA data were collected to determine if similar peaking in the HAA concentrations likewise occurred. These results imply that additional work focused on pH 7-8 and Cl_2/N mass ratios commonly used in practice (3, 4, and 5/1) is warranted to obtain a more complete understanding of the role of pH and Cl_2/N ratio in HAA formation.



Source: Diehl *et al*., 2000.

Figure 2-1 – DOX concentrations in Lake Austin water as a function of pH and Cl_2/N mass ratio

2.2.2. Bromide

Available data (Cowman and Singer, 1996; Symons *et al*., 1998; Singer *et al*., 1999; Zhang *et al*., 1999; Diehl *et al*., 2000) indicate two effects of elevated bromide concentrations on HAA formation. First, the speciation shifts toward the bromine-substituted HAAs, in particular the bromine-substituted DXAAs. Formation of bromochloroacetic acid (currently an unregulated HAA) is favored over formation of dibromoacetic acid. Second, the total HAA concentration on a mass basis increases somewhat. Cowman and Singer (1996) found that Myrtle Beach extracts provided a constant molar yield of HAAs with increasing bromide concentration, so the increase in mass concentration may be largely reflective of bromine's greater molecular weight compared to chlorine's. In general, mid-range bromide concentrations (0.05 to 0.1 mg/L) cause a small increase in HAA mass concentrations (10-30%).

2.2.3. Temperature

Most of the DBP formation work during chloramination has been done at constant temperature. Singer *et al*. (1999) incubated samples at 20°C, while Symons *et al*. (1998) used 22°C. Clearly, it is reasonable to expect HAA concentrations to increase with increasing temperature because of faster reaction kinetics. For example, Roth and Ozment (1999) showed an approximate doubling of HAA concentrations (14 to 28 µg/L) in the Carbondale, IL distribution system when the water temperature increased from 8°C to 24°C. The treatment plant uses both free chlorine and chloramines, so the kinetic effects on both disinfectants are reflected in the data. A review of Information Collection Rule (ICR) data (EPA, 2000) for surface water treatment plants in the southern half of the U.S. known to be practicing chloramination likewise shows elevated HAA concentrations for the July/September samples in comparison to the October/December samples. In some cases, the HAA concentrations in the summer samples were twice those in the fall samples. Clearly, additional research on HAA formation at elevated temperatures is needed based on the significant temperature effect suggested by the available data.

2.2.4. Precursor Type and Concentration

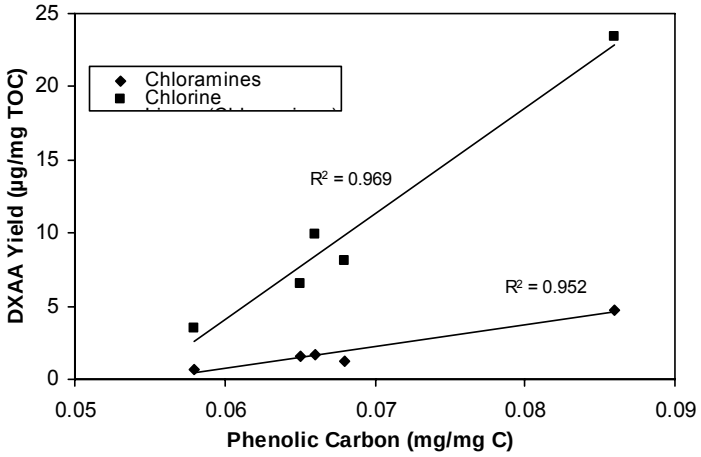
Only a limited amount of work has been done on the role of precursor type and reactivity in DBP formation. Symons *et al*. (1998) studied a series of source waters of low to medium specific ultraviolet absorbance (SUVA). Singer *et al*. (1999) studied five source waters with a broad range of SUVA values, as well as hydrophobic extracts from these waters. The impact of ozonation and conventional treatment (*i.e*., coagulation, flocculation, settling, and filtration) separately and together also was examined for a subset of the source waters and extracts. For untreated hydrophobic extracts, DXAA yield (µg DXAA/mg TOC) was highly correlated to the phenolic carbon content for both

chlorination and chloramination (Figure 2-2). As expected, NOM reactivity, as quantified by DXAA yield, was much greater with chlorine than with chloramines.

Phenolic carbon could only be measured on untreated extracts; correlations with SUVA must be examined for the treated extracts. Unfortunately, SUVA measurements are available for only three of the five treated extracts examined by Singer *et al*. (1999). DXAA yield in the hydrophobic extracts likewise was highly correlated to SUVA for both chlorination and chloramination (Figure 2-3). Ozonation prior to chloramination decreased SUVA, as would be expected, but did not significantly affect DXAA yield. Thus, the slope of the DXAA yield versus SUVA plot changed substantially (Figure 2-3), but destruction of UV-absorbing characteristics (presumably double bonds and aromaticity) had little effect on DXAA formation, suggesting that these UV-absorbing NOM sites were not DXAA precursor sites. The good correlation between DXAA yield and SUVA and the absence of an effect on DXAA yield by SUVA removal through ozonation seem somewhat contradictory, indicating that much more exploration of the reactivity of various NOM fractions is needed to better understand the role of NOM in DXAA formation.

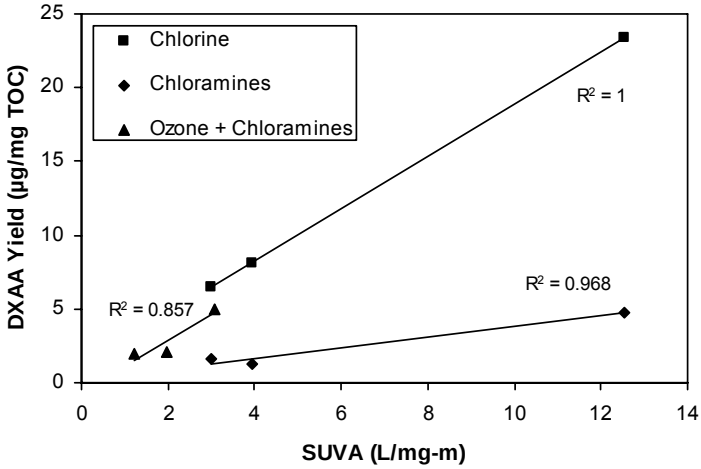
The correlation between DXAA yield and SUVA is not as good for source waters ($R^2 < 0.7$) as for hydrophobic extracts ($R^2 > 0.85$) (Figure 2-4); nevertheless, a relationship between DXAA yield and SUVA is suggested. For the waters studied by Singer *et al*. (1999), conventional treatment significantly decreased the TOC concentration, as expected, but only decreased SUVA in one of the three waters for which data are available. The DXAA yield decreased by approximately 20% in two of the waters and by 45% in the third. Overall, the combination of a lower TOC concentration and a lower DXAA yield had a substantial impact on the DXAA concentration, which was 20 to 30% of that formed when the source waters were

chloraminated. Thus, as with chlorination, removal of NOM in treatment processes has a positive impact on DBP formation.



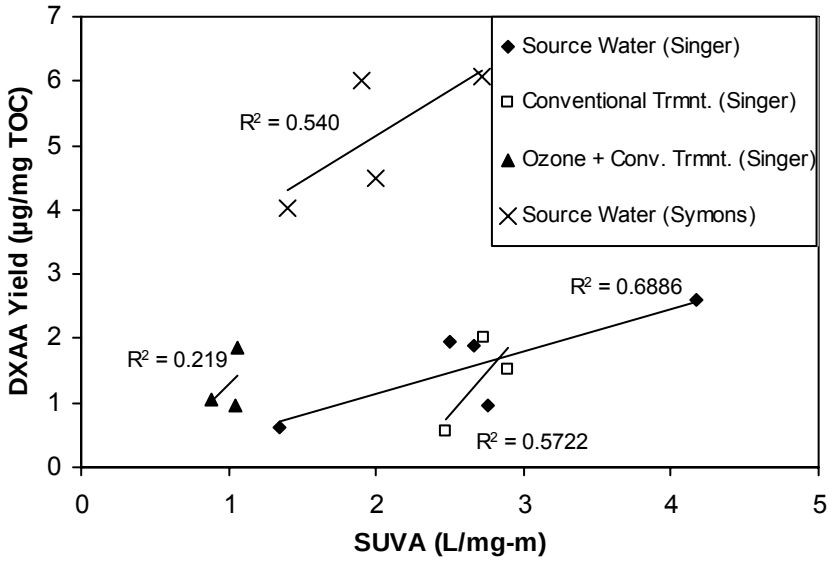
Source: Data from Singer *et al*., 1999.

Figure 2-2 – Reactivity of extracts versus phenolic carbon. Chloramination conditions: pH 8, 20°C, 4/1 Cl_2/N, and a 2 mg/L residual as Cl_2 after 24 hours; chlorination conditions: pH 8, 20°C, and a 1 mg/L residual as Cl_2 after 24 hours.



Source: Data from Singer *et al*., 1999.

Figure 2-3 – Reactivity of extracts versus SUVA. Chloramination conditions: pH 8, 20°C, 4/1 Cl_2/N, and a 2 mg/L residual as Cl_2 after 24 hours; chlorination conditions: pH 8, 20°C, and a 1 mg/L residual as Cl_2 after 24 hours; ozone + chloramination: ozonation at pH 7 and O_3:TOC = 1:1, and chloramination at pH 8, 20°C, and a 2 mg/L residual as Cl_2 after 24 hours.



Source: Data from Singer *et al*., 1999 and Symons *et al*., 1998.

Figure 2-4 – Chloramine reactivity of bulk water versus SUVA. Chloramination conditions (Singer): pH 8, 20°C, 4/1 Cl_2/N, and a 2 mg/L residual as Cl_2 after 24 hours; ozone + chloramination conditions (Singer): ozonation at pH 7 and O_3:TOC = 1:1, and chloramination at pH 8, 20 °C, and a 2 mg/L residual as Cl_2 after 24 hours; Chloramination conditions (Symons): pH 8, 20°C, 5/1 Cl_2/N, and a 2 mg/L residual as Cl_2 after 48 hours

Preozonation before conventional treatment substantially decreased SUVA relative to both that of the source water and for conventional treatment alone, which is essentially the same effect as seen with the hydrophobic extracts (Figure 2-3). The impact of ozonation on DXAA formation was not as clear cut. The DXAA yield decreased in two waters and increased in one relative to conventional treatment, while TOC removal increased in two waters and decreased in one. As a result, DXAA formation was about the same as with conventional treatment in two waters and less than that observed with conventional treatment in the third water. The benefits of ozonation are uncertain based on the work of Singer *et al*. (1999), but additional pilot and full-scale

data presented below provide stronger evidence for ozone's positive effect on reducing HAA formation.

The DXAA yield for four of the source waters studied by Symons *et al*. (1998) also is shown in Figure 2-4. The strength of the correlation between DXAA yield and SUVA was the same as for the data of Singer *et al*. (1999); however, the DXAA yield was much greater. The data for both projects were collected at pH 8, but both the Cl_2/N mass ratio (5/1 vs. 4/1) and the incubation times (48 vs. 24 hr) were larger in the work of Symons *et al*. (1998). Interpretation of the results is confounded by the different incubation periods, but the data at least suggest that the relationship between DXAA yield and SUVA may be significantly influenced by chloramination conditions, which would be expected based on the discussion above dealing with the significance of pH and Cl_2/N ratio.

Natural organic matter typically consists of hydrophobic (humic) substances and hydrophilic (nonhumic) substances. Teng and Veenstra (1996) studied the reactivity of different apparent molecular weight fractions of hydrophilic and hydrophobic organics isolated from Kaw Reservoir, Oklahoma water. Precursors in the 1,000 to 10,000 molecular weight fraction produced more HAAs than the other molecular weight fractions studied; however, the < 1,000 molecular weight fraction produced the greatest DCAA yield. In addition, chloramination of hydrophobic fractions exhibited greater DCAA yields than hydrophilic fractions. Hwang *et al*. (2000) fractionated and isolated five NOM fractions (hydrophobic, transphilic, hydrophilic acid plus neutral, hydrophilic bases, and colloids) from the Colorado River, which is a low-humic water. These waters were chloraminated at a 5/1 Cl_2/N mass ratio to yield a total chlorine residual of 2 mg/L after a 24-hour incubation at pH 8. Chloramination of Colorado River source water resulted in predominantly DXAA formation, but yielded only 6.2 percent of the total

HAAs that formed during chlorination. The hydrophilic, transphilic, and hydrophobic fractions all contributed significantly in terms of HAA yield. However, the hydrophilic acid plus neutral fraction exhibited the greatest HAA yield. This fraction was nearly six times as reactive as the hydrophobic fraction, accounting for approximately 49% of the total yield from the isolated NOM fractions. In addition, the hydrophilic fractions (hydrophilic acid plus neutral and hydrophilic bases) represented approximately 76% of the total yield of the isolated NOM, while the hydrophobic fraction only accounted for about 9%, indicating that treatments to minimize HAA formation in low-humic waters should address the removal of polar NOM fractions.

DBP precursors can be removed by treatment processes such as alum coagulation, softening, and filtration. However, the extent of precursor removal by these treatment processes varies considerably. Coagulation has been shown to preferentially remove hydrophobic and higher molecular weight NOM more effectively than other NOM constituents (Collins *et al*., 1986; Krasner and Amy 1995; White *et al*., 1997). In addition, White *et al*. (1997) determined that alum reacts preferentially to remove hydrophobic NOM, and that greater amounts of hydrophilic NOM are removed only after the coagulant demand of the hydrophobic NOM has been satisfied. Softening is also capable of achieving significant NOM removal (Liao and Randtke, 1985; Thompson *et al*., 1997; Smith *et a*l., 2004), typically removing NOM with high molecular weights (Liao and Randkte, 1985; Semmens and Staples, 1986; and El-Rehaili and Weber, 1987).

2.2.5. Chloramine Residual Concentration

Symons *et al*. (1998) studied the impact of chloramine residual concentration on DBP formation (*i.e*., DOX, THMs, HAAs, and CNX) in three source waters. Over a broad range of pH and Cl_2/N ratios, no relationship between residual concentration (1, 2, and 4 mg/L) and DBP formation was apparent in 48-hour simulated distribution system

(SDS) tests. More rigorous statistical analyses of this extensive data set also failed to show any statistically significant relationship between DBP formation and chloramine residual concentration (Diehl 2001). Thus, the available data suggest that residual concentration is of secondary importance in DBP formation over the range of concentrations typical in practice. Symons *et al*. (1998) only studied a 48-hour incubation period, however, which may have failed to capture kinetic effects of chloramine concentration that might be apparent at shorter incubation periods.

2.2.6. Modes of Chloramine Addition

Although chloramination seems, at first glance, to be relatively straightforward, it has been implemented in practice in a wide variety of ways, which can lead to significant differences in DBP formation among utilities practicing chloramination. The traditional approach to chloramination involves the addition of ammonia and chlorine simultaneously (or nearly so) very early in the treatment train, usually at the rapid mix basin. Mixing might be less than perfect and chemical addition might not be truly simultaneous, with the possible presence of free chlorine being an obvious concern with respect to DBP formation. Symons *et al*. (1998) studied the effects of delayed ammonia addition (versus preformed chloramines) and mixing intensity to simulate the less than perfect conditions that might be encountered at full scale. A 30-second delay between chlorine and ammonia addition produced no significant effect on DBP concentrations or speciation after 48 hours of incubation; in particular, no discernable impact on HAA formation was evident. Therefore, the formation kinetics appear slow enough such that very short periods of free chlorine exposure will have no effect on DXAA concentrations at the longer time frames of regulatory interest. These results also provide confidence that the common practice of using preformed chloramines in bench-scale studies does not introduce troubling artifacts into the data.

Increasingly, utilities are not practicing traditional chloramination. Many plants now have a significant period of free chlorination prior to ammonia addition for purposes of meeting CT requirements. For example, Seidel *et al*. (2000) evaluated ICR data for 70 plants practicing chloramination. Of these, only 9 used chloramination alone, while the remainder used a combination of chlorine and chloramination. Similarly, a recent survey of medium and large utilities found that that 42 of 58 plants added ammonia after chlorine, with an average lag time of 25.7 minutes for ammonia addition (Connell *et al*., 2000). In practice, the lag time between chlorine and ammonia can range from a few minutes to several hours. As might be expected, significant exposure to free chlorine will produce greater DBP formation than with chloramines alone. For example, Symons *et al*. (1998) studied an unfiltered lake water from the Pacific Northwest in which ammonia addition occurred 2 to 5 hours after chlorine addition. A sample from the distribution system showed an HAA_6 concentration of 38 μg/L, while bench-scale chloramination of the source water with preformed chloramines produced a concentration of only 8 μg/L. Rajbhandari *et al*. (1999) studied the impact of free chlorine contact time on Manatee Lake water from southwest Florida and Mississippi River water from Minneapolis, Minnesota. These settled waters were prechlorinated for 0.25, 1, or 3 hours prior to ammonia addition to achieve a 4.5/1 Cl_2/N mass ratio and a 3 mg/L 24-hour target chloramine residual. Increasing free chlorine contact times caused both an increase in the chlorine required to meet the target residuals as well as an increase in HAA_9 (Table 2-2). Thus, brief exposure to free chlorine that may result from mixing inefficiencies or slightly staggered chlorine and ammonia addition points is not the major issue with respect to free chlorine exposure in chloramination. Rather, significant periods of free chlorination prior to ammonia addition necessitated by disinfection regulations are a far greater concern with respect to DBP formation. Many utilities now face a

chlorine/chloramines/CT balancing act that will only get more difficult in the future. In many respects, the rate of DBP formation during chloramination is the key issue (i.e., how much additional DBP formation will occur in the treatment plant and distribution system after chlorination is terminated by ammonia addition?). Therefore, a better understanding of DXAA formation kinetics with chloramines is needed as an important input to the complicated decision-making process facing some utilities.

Table 2-2 – Impact of free chlorine contact time on HAA formation

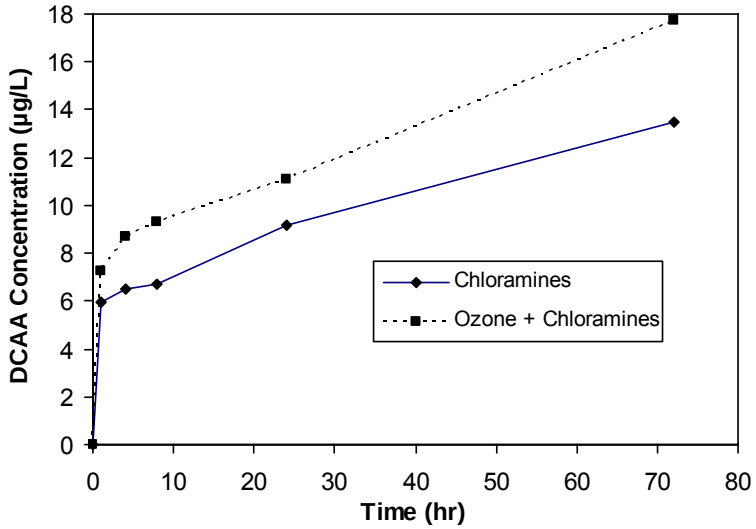
Water	Treatment	FCCT (hr)	FC_0 (mg/L)	HAA_9 (µg/L)
Manatee Lake Water	Settled	0.25	6.5	50
		1	7.6	56
		3	8.2	69
Mississippi River Water	Settled	0.25	4.5	26
		1	5.0	49
		3	6.0	56

Source: Data from Rajbahandari *et al*., 1999.

FCCT – free chlorine contact time; FC_0 – initial free chlorine dose

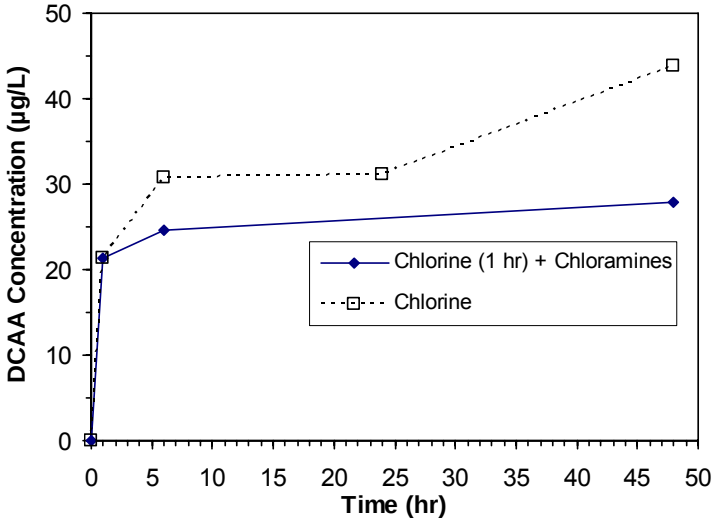
Unfortunately, kinetic data are very limited for DXAA formation during chloramination. Singer *et al*. (1999) studied the kinetics for one hydrophobic extract with and without ozonation before chloramination (Figure 2-5). A period of relatively rapid dichloroacetic acid (DCAA) formation occurred over the first hour, with a much slower rate of formation thereafter. Although the extent of formation is much less than with chlorine, the shape of the curve is very similar to that observed with chlorination DBPs: rapid initial formation followed by a decreased rate of formation. Of particular interest in this regard is whether or not an initial chlorination step would "consume" all the rapidly-reacting NOM material resulting in only a slow rate of DXAA formation during a subsequent chloramination step. Only very limited data are available on the DBP

formation kinetics of chlorine and chloramine combinations. Long *et al*. (1992) examined DCAA formation with chlorine alone and with 1 hour of chlorination followed by chloramination (Figure 2-6). These data suggest that the rapidly-reacting NOM was "consumed" during the chlorination step, with further DCAA formation occurring at a slow rate during subsequent chloramination (*i.e*., data after 1 hour). Carlson *et al*. (1996) evaluated the potential of continued HAA formation in distribution systems by dosing treated water with chlorine and allowing it to react for a short time prior to ammonia addition at a 5/1 Cl_2/N mass ratio. HAAs were measured immediately after ammonia addition and again after 13 days of storage. Approximately 86% of the total HAA formation formed prior to ammonia addition, indicating minimal additional HAA formation occurs after chloramination. Dickenson *et al*. (2002) determined the influence of chlorine dose, pH, and temperature on HAA formation kinetics during short periods of chlorination. HAAs were measured 5, 10, and 30 minutes after dosing, and in a source water from Boulder, CO, increasing the chlorine dose 66% resulted in approximately a 66% increase in HAA formation at all three incubation times. They also found that waters incubated at pH 5 and 8 resulted in similar amounts of HAA formation, whereas water incubated at pH 10 had significantly less, and that temperature had a minimal influence on short-term HAA formation. A much more detailed assessment of DXAA formation kinetics during chloramination and the impact of prechlorination on these kinetics is needed, however, to truly clarify the matter.



Source: Data from Singer *et al*., 1999.

Figure 2-5 – DCAA formation kinetics. Chloramination conditions: pH 8, 20°C, 4/1 Cl_2/N, and a 2 mg/L residual as Cl_2 after 24 hours; ozone + chloramination: ozonation at pH 7 and 3.17 mg/L O_3 dose, and chloramination at pH 8, 20 °C, and a 2 mg/L residual as Cl_2 after 24 hours.



Source: Data from Long *et al*., 1992.

Figure 2-6 – Chlorination and chloramination kinetics. Chlorine dosed in samples buffered to pH 6 to achieve a 1 mg/L residual as Cl_2; secondary disinfection by chloramines: samples buffered to pH 8.25 (after chlorination at pH 6 for 1 hour) dosed to achieve a 3/1 Cl_2/N ratio and a 2 mg/L residual as Cl_2.

Another approach to recent concerns about disinfection and DBP control is the implementation of ozonation as the primary disinfectant, with chloramines used as a secondary disinfectant to maintain a residual in the distribution system. Much of the available data indicate that the combination of ozonation and chloramination is better than chloramination alone in controlling HAA formation. Symons *et al*. (1998) conducted pilot studies with ozone on two source waters (Table 2-3). The addition of preozonation to both conventional lime softening and conventional alum treatment significantly decreased HAA formation in 48-hour simulated distribution system (SDS) tests on the finished water. Lykins *et al*. (1994) studied different disinfection schemes for Mississippi River water that was coagulated, settled, pre-disinfected, sand filtered, and post-disinfected to simulate distribution system conditions (Table 2-4). A dramatic decrease in HAA formation was observed in switching from chlorine to chloramines, and a further decrease resulted from the introduction of ozonation, followed by chloramination after GAC filtration. Jacangelo *et al*. (1989) conducted pilot and full-scale studies on several surface waters (Table 2-5). Switching from chloramination to the combination of ozonation and chloramination decreased HAA formation in three water sources, although to varying extents. In the first water, the large decrease in HAA formation can be attributed to the elimination of a 4-hour period of free chlorination in the chloramination treatment scheme. The large decrease in the HAA formation in the second water may have resulted from the relatively large ozone dose (1.45 mg O_3/mg TOC). A much smaller decrease in HAA formation occurred in the third water with a more realistic ozone dose of 0.51 mg O_3/mg TOC.

Although the bench-scale results of Singer *et al*. (1999) are equivocal about the benefits of preozonation in decreasing HAA formation upon subsequent chloramination, the other available data consistently indicate preozonation decreases HAA formation. In

fact, Symons *et al*. (1998) recommended the introduction of ozonation if DBP formation could not be controlled through chloramination alone.

Table 2-3 – Impact of ozone on HAA formation in pilot studies of Symons *et al*. (1998)

Operating Condition	Cl_2/N Mass Ratio	Incubation pH	HAA_6 (µg/L)
Lake Austin Water:			
Conventional Lime Softening	5/1	8	9.6
Preozonation & Conv. Lime Softening	5/1	8	1.4
California State Project Water:			
Conventional Alum	5/1	8	15
Preozonation & Conv. Alum	5/1	8	2.6
Pre-O_3, Conv. Alum, & Biofiltration	5/1	8	2.4

Table 2-4 – Jefferson Parish (LA) pilot plant SDS HAAs

Disinfectant(s)	Incubation pH	TOC* (mg/L)	HAA_6†,‡ (µg/L)
Pre- & Post-Chlorine§	7-8	3.2	146
Pre- & Post-Chloramines	7-8	3.2	14
Pre-Ozone, Post Chloramines	7-8	2.9	8.7

Source: Data from Lykins *et al*., 1994.

* Concentration in disinfection contact chamber effluent.

† Five-day simulated distribution system incubation time.

‡ Ambient bromide concentration not reported, but HAA_6 speciation suggests relatively low bromide concentration.

§ Pre-disinfection occurred before sand filtration; post-disinfection after sand filtration.

Table 2-5 – Impact of changes in disinfectants on HAA formation

Disinfectant Change	TOC (mg/L)	O_3 (mg/L)	Cl_2/N Mass Ratio	Br^- (µg/L)	pH	Decrease in HAA_5 Concentration (%)
NH_2Cl^* to O_3 & NH_2Cl	2.46	2.0	5.9/1	150	8.2	80
NH_2Cl to O_3 & NH_2Cl	5.51	8.0	5.0/1	230	9.3	64
NH_2Cl to O_3 & NH_2Cl	3.91	2.0	4.2/1	320	7.8	16

Source: Data from Jacangelo *et al*., 1989.

* Four-hour delay between chlorine and ammonia addition; no delay with ozonation. Chlorine and ammonia added concurrently for all other cases.

2.3. HALOAMINE CHEMISTRY

2.3.1. Chloramines

Chloramine chemistry is complicated because of the several species of combined and free chlorine that may be present and because chloramines are inherently unstable and decay through a complex set of reactions that result in the oxidation of ammonia and the formation of chloride. An understanding of this chemistry is essential to an improved understanding of DBP formation during chloramination. Jafvert and Valentine (1992) proposed a model of chloramine decomposition kinetics for a broad range of Cl_2/N ratios and concentrations. Valentine *et al*. (1998) and Vikesland *et al*. (2001) narrowed the focus of the model to address conditions typical of chloramination practice in drinking water treatment. The significant chloramine reactions under drinking water conditions are listed in Table 2-6.

Reactions 1 to 4 represent the substitution (1 and 3) and hydrolysis (2 and 4) reactions between HOCl and ammonia or the chloramines. Reactions 5 and 6 represent the disproportionation reactions of the chloramine species. Reactions 7 through 10 represent the redox reactions that occur in the absence of measurable levels of free

chlorine. The overall rate of chloramine decomposition near neutral pH and above is limited by the rate of formation of dichloramine, which then rapidly decomposes. The rate of monochloramine loss increases as the solution pH decreases because of the enhanced rate at which dichloramine forms at lower pH values (Vikesland *et al*., 2001). Dichloramine formation occurs in two ways: (1) through monochloramine hydrolysis (Reaction 2) and subsequent monochloramine reaction with free chlorine (Reaction 3) and (2) through monochloramine disproportionation (Reaction 5). Reaction 5 is a net reaction, which consists of an equilibrium reaction producing monochlorammonium ion (NH_3Cl^+), followed by a reaction between this species and monochloramine. Reaction 5 is general acid catalyzed; therefore, a variety of proton-donating species can act to accelerate the reaction rate. General acid catalysts include the acid forms of carbonate, phosphate, and sulfate, as well as acetic acid (Vikesland *et al*., 2001). Of practical significance in drinking water treatment, the rate of chloramine decay shows a positive concentration dependence on alkalinity (*i.e*., bicarbonate) and natural organic matter (*i.e*., organic acids present in humic and fulvic materials) (Valentine *et al*., 1998). At free ammonia concentrations of less than 1 to 2 mg/L, Reactions 2 and 3 are the dominant pathway for dichloramine formation, while Reaction 5 dominates at higher ammonia concentrations. Under typical drinking water treatment conditions (neutral pH or above and Cl_2/N mass ratios of 3-5/1), monochloramine is the primary species present; free chlorine, dichloramine, and monochlorammonium ion are present at very low concentrations.

Table 2-6 – Chloramination reactions of importance in drinking water treatment

No.	Reaction
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$
2	$NH_2Cl + H_2O \rightarrow NH_3 + HOCl$
3	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$
4	$NHCl_2 + H_2O \rightarrow NH_2Cl + HOCl$
5	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$
6	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$
7	$NH_2Cl + NHCl_2 \rightarrow N_2 + 3H^+ + 3Cl^-$
8	$NH_2Cl + H_2O \rightarrow I$
9	$I + NH_2Cl \rightarrow HOCl +$ products
10	$I + NHCl_2 \rightarrow$ products

"I" is an unidentified reactive intermediate; "products" refers to a combination of nitrogen gas, ammonia, chloride, nitrate and unknown products.

2.3.2. Brominated Species

Bromide is widespread in source waters. Amy *et al*. (1994) found an average concentration of 100 μg/L in the U.S. with a range of 0 to 2.3 mg/L. The presence of bromide substantially complicates haloamine chemistry because both HOCl and monochloramine react with bromide forming a variety of products. A summary of the important reactions is provided in Table 2-7. When chlorine is added to water containing ammonia and bromide, Reactions 1 and 11 proceed rapidly in parallel, with the $[NH_3]/[Br^-]$ ratio largely determining which reaction dominates (Bousher *et al*., 1989). Under drinking water treatment conditions, Reaction 1 dominates, so limited HOBr formation occurs, largely because of the very low HOCl concentration (Valentine *et al*., 1998). The rate constant for Reaction 1 is much larger than for Reaction 11 (Jafvert and Valentine 1992; White 1999), but NH_4^+ dominates at typical pH values, resulting in a low

NH_3 concentration. The resulting ratio of reaction rates between Reactions 1 and 11 is on the order of 100:1 for waters with moderate to high bromide concentrations, demonstrating that HOBr formation is not negligible under these conditions. Once formed, HOBr can participate in several reactions. It can react with ammonia to form monobromamine (Reaction 17) and with monochloramine to form bromochloramine (Reaction 12). The rate constant for Reaction 17 is 7.5 x 10^7 $M^{-1}s^{-1}$ (Wajon and Morris 1980), while the rate constant for Reaction 12 is 2.86 x 10^5 $M^{-1}s^{-1}$ (Gadza and Margerum 1994). Although these rate constants are quite different, under typical conditions the relative concentrations of NH_3 and NH_2Cl may result in comparable reaction rates for Reactions 17 and 12.

Table 2-7 – Bromide-chloramine reactions of importance in drinking water treatment

No.	Reaction
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$
11	$HOCl + Br^- \rightarrow HOBr + Cl^-$
12	$HOBr + NH_2Cl \rightarrow NHClBr + H_2O$
13	$NH_2Cl + H^+ \leftrightarrow NH_3Cl^+$
14	$NH_3Cl^+ + Br^- \rightarrow NH_3Br^+ + Cl^-$
15	$NH_3Br^+ \leftrightarrow NH_2Br + H^+$
16	$NH_3Br^+ + NH_2Cl \rightarrow NHClBr + NH_4^+$
17	$HOBr + NH_3 \rightarrow NH_2Br + H_2O$
18	$NH_2Br + NH_2Br \leftrightarrow NHBr_2 + NH_3$
19	$NH_2Br + NHBr_2 \rightarrow$ Products
20	$NHBr_2 + NHBr_2 + H_2O \rightarrow$ Products
21	$2NHClBr + H_20 \rightarrow N_2 + HOBr + 2HCl + HBr$

Monochlorammonium ion, formed by the ionization of monochloramine (Reaction 13), also reacts with bromide to form monobromammonium ion (Reaction 14). NH_3Br^+ is a strong acid and dissociates to monobromamine (Reaction 15); NH_3Br^+ also

reacts with monochloramine to form bromochloramine (Reaction 16). Monobromamine is rapidly consumed as a result of Reactions 15 and 16, as well as disproportionation reactions (Reactions 18-20), so its concentration should be very low (Bousher *et al*., 1989). Bromochloramine also can be formed by the reaction of HOBr with monochloramine (Reaction 12); however, Reaction 16 dominates under drinking water conditions (Vikesland *et al*., 2001). Valentine (1983) proposed that bromochloramine decomposes to nitrogen gas, chloride, bromide, and HOBr (Reaction 21).

Under typical drinking water treatment conditions, bromide oxidation by monochlorammonium usually dominates (Reaction 14) in comparison to the reaction between bromide and the free chlorine produced by monochloramine hydrolysis (Reaction 11) (Vikesland *et al*., 2001). Reaction 14 produces monobromammonium, which undergoes rapid reactions to produce bromochloramines, primarily NHClBr (Valentine 1986 and Vikesland *et al.,* 2001). NHClBr, therefore, is expected to be the bromine-containing species present at the highest concentration (Bousher *et al*., 1989; Vikesland *et al*., 2001), while smaller concentrations of bromamines and HOBr are expected. Because of their relative insignificance, all the reactions involving NH_2Br and NBr_3 are not included in Table 2-7, but can be found in Bousher *et al*. (1989).

The reactions of the bromamines and bromochloramines are generally much faster than those of the chloramines. For example, the half-life of dibromamine at pH 8 is 30 minutes and that of monobromamine is 19 hours (Wajon and Morris, 1980), whereas a half-life of 50 to 100 hours is typical for monochloramine (Jafvert and Valentine, 1992). The more rapid kinetics of bromine-containing haloamines means that these compounds do not accumulate to an appreciable extent and are present at substantially lower concentrations than monochloramine (Vikesland *et al*., 2001). From the viewpoint of monochloramine stability, bromide can be viewed primarily as a catalyst that increases

the rate of monochloramine decomposition in drinking water (Vikesland *et al*., 2001; Diehl *et al*., 2000). From the viewpoint of DBP formation, bromide can be viewed as substantially increasing the range of possible halogenating species, with bromochloramine, mono- and dibromamine, and free bromine, being the main chemicals of interest.

2.3.3. Haloamine Reactions with NOM

Two types of reactions can be identified between monochloramine and NOM. In the first, NOM catalyzes auto-decomposition of monochloramine through general acid catalysis, which results in the oxidation of ammonia. The second involves reduction of active chlorine through oxidation and substitution reactions with NOM. The presence of NOM clearly accelerates the rate of monochloramine decay, and either or both of the reaction types identified could account for the observed acceleration. Valentine *et al*. (1998) and Vikesland *et al*. (1998) investigated the relative significance of the two reaction types in controlled experiments in which chlorine and nitrogen mass balances were examined. These experiments demonstrated that NOM accelerates monochloramine decay primarily because NOM is readily oxidized; the role of NOM as a catalyst is negligible. The total production of the typical monochloramine oxidized decay products, nitrogen gas and nitrate, decreases in the presence of NOM, and the production of the isoelectronic decay product, ammonia, increases. This observation reflects the fact that the oxidizing power of monochloramine is used to oxidize NOM to various oxidized organic species at the expense of oxidizing nitrogen. The production of chloride is largely unaffected by the presence of NOM, indicating that the same extent of oxidation occurs with and without NOM. This result further supports the conclusion that NOM is oxidized by monochloramine. Nitrate formation increases in the presence of NOM,

indicating that NOM causes a shift in product speciation away from nitrogen gas and toward nitrate.

These overall observations of NOM reactivity with monochloramine are likewise in agreement with more specific analyses that have identified formation of various DBPs as a result of monochloramine/NOM reactions (Speitel, 1999). DBP formation might result from reactions with monochloramine or through general acid catalysis reactions with monochlorammonium ion. In particular, Snyder and Margerum (1982) and Issac and Morris (1983) showed that general acid catalysis reactions could transfer chlorine to nitrogenous organic chemicals at significant reaction rates through pH values as high as 8 to 8.5. Vikesland *et al*. (1998) suggest that NOM may contain two types of reactive sites: those that readily react with monochloramine and those that react only with the HOCl produced by monochloramine hydrolysis (Reaction 2). They further suggest that chloramination DBPs that are likewise formed during chlorination may result from reactions between NOM and the HOCl formed by monochloramine hydrolysis. Conversely, DBPs found primarily during chloramination may result from reactions between NOM and monochloramine (or monochlorammonium ion). Duirk *et al*. (2005) accurately modeled monochloramine loss in the presence of NOM by assuming that it reacts via a biphasic reaction. They postulated that the initial fast period of formation was a result of monochloramine reacting with NOM, and the slow long-term period of formation was a result of HOCl produced from monochloramine hydrolysis reacting the NOM. This model was also extended to predict DCAA formation by assuming it to be directly proportional to the amount of active chlorine (monochloramine and free chlorine) that reacts with NOM (Duirk *et al*., 2006).

The formation of DBPs through reactions between bromine-containing haloamines and NOM has not been studied in detail, although the observed formation of

bromine-substituted HAAs in the presence of bromide clearly indicates that such reactions are of practical importance. As noted above, bromochloramine is the species present at highest concentration under typical drinking water conditions; thus, it is the most likely brominating agent. Valentine (1986) found that bromochloramine reacts rapidly with *N*,*N*-diethyl-*p*-phenylenediamine (DPD), indicating that the bromine atom of bromochloramine is very labile and reactive. This rapid reactivity led Valentine (1986) to suggest that the products of bromochloramine/NOM reactions should be characteristic of those produced by free bromine. Little formation of THMs was found with dibromamine (Sugam and Helz, 1980), suggesting similar low reactivity for both chloramines and bromamines with respect to THM formation. The suggestion by Vikesland *et al*. (1998) that different types of reactive sites exist in NOM presumably can be extended to suggest that some DBP formation also may result from reactions between NOM and HOBr. Duirk *et al*. (2002) studied the effect of bromide ion on monochloramine loss in the presence of natural organic matter in Iowa River water. Bromide ion catalyzes monochloramine autodecomposition by the formation of active bromine intermediates. However, in the presence of NOM, the active bromine may either react with NOM or monochloramine. From model development and experimental data collected, they hypothesized that most of the active bromine reacts with the NOM via oxidative and substitution reactions and not with monochloramine. A significant quantity of bromide appears to be incorporated into the NOM resulting in the formation of more brominated species. A better understanding of the reaction pathways of the bromine-substituted oxidant will help to better predict the formation of bromine-substituted HAAs.

2.4. SUMMARY

The literature indicates that many factors may influence HAA formation during chloramination. Unfortunately, the relative importance of these factors remains unclear.

The focus of previous studies was either on overall DBP formation because the significance of HAA formation was previously unknown, or on the use of chloramine as a secondary disinfectant, limiting the chloramination conditions studied. Therefore, further investigation into how operating conditions affect HAA formation during chloramination is warranted. Also, the available data on precursors from various water sources and their concentrations are inadequate for the purposes of understanding the reactivity of NOM and various key fractions of NOM, as well as the effects of treatment on those fractions, both from the viewpoint of their removal and their resulting reactivity after treatment. Additionally, kinetic data are very limited for DXAA formation during chloramination, and many plants have incorporated a significant period of chlorination prior to ammonia addition for purposes of meeting CT requirements, which has an unknown effect on DXAA formation during subsequent chloramination.

This research provides a more detailed assessment of the relative importance of several variables that have been shown to influence HAA formation, as well as a detailed assessment of HAA formation kinetics during chloramination and the impact of prechlorination on these kinetics. In addition, when bromide is present, bromine-substituted haloamines are formed, which produce bromine-substituted haloacetic acids; the number of chemical species that may be relevant in controlling DXAA formation is greatly increased; and our ability to predict DXAA formation and speciation is hampered considerably. Until a better understanding of haloamine speciation and reactivity under conditions typical of practice is achieved, the formulation of better strategies for minimizing the formation of DXAAs (and other disinfection by-products) will be hampered. Therefore, this research also provides insight into haloamine speciation and reactivity.

CHAPTER 3: Materials and Methods

3.1. WATER COLLECTION, TREATMENT FRACTIONATION AND STORAGE

3.1.1. Source, Collection, and Storage

Water was collected from five different sources: Lake Austin, Metedeconk River, a reservoir near Charleston, S.C., Biscayne Aquifer, and reservoirs near St. Paul, MN. These source waters provided a range of naturally occurring organic matter, bromide, alkalinity, and SUVA, which allowed the study of the significance of source water variability both spatially and temporally on HAA formation.

To ensure consistency of results, large volumes of water were obtained and stored at 4°C until used. Periodic measurements were made of pH, alkalinity, TOC, and UV_{254} to provide information on the stability of water during storage.

3.1.1.1 Lake Austin

Water was collected from Lake Austin, the drinking water source for the city of Austin, Texas. The water was collected immediately following the raw water intake pumps prior to chlorination at the Ullrich Water Treatment Plant, a chloramination plant that practices softening.

3.1.1.2 Metedeconk River

Brick Utilities primarily draws its water from the Metedeconk River in New Jersey, which is treated by alum coagulation. Source water samples (30 L) were collected for characterization, treatment, fractionation, and storage. This source water, however, was not stable during long storage periods, and therefore was only stored for up to 1 month at 4 °C.

3.1.1.3 Charleston

The Hanahan Water Treatment Plant in Charleston, South Carolina primarily draws its water from the Bushy Park Reservoir and the Edisto River. This plant is a conventional coagulation plant with disinfection occurring after filtration in a disinfection contact basin where chlorine is added as the water enters and ammonia as it exits. The plant's treatment train allowed the collection of 30-L samples of both source and filtered water prior to any disinfectant addition.

3.1.1.4 Biscayne Aquifer

Boca Raton, Florida draws its water from the Biscayne aquifer. The water is lime softened and settled; chlorine is added before the multimedia filters, allowing for 10 – 20 minutes of contact time before ammonia addition at a transfer pump station prior to the clearwells. This treatment train allowed the collection of 30-L samples of both source and settled water without any disinfectant added.

3.1.1.5 St. Paul

The St. Paul Water Utility draws water from a series of impoundments fed by diverted Mississippi River water and water shed runoff. This plant is a combined lime softening and alum coagulation plant in which chlorine is added three minutes before ammonia after the water is softened/coagulated, flocculated and settled. 30-L samples of source and settled water were collected, again prior to disinfectant addition.

3.1.2. Treatment and Fractionation

3.1.2.1 Softening

The treatment plants that serve the city of Austin currently add chlorine in the transmission lines from their source water intakes; therefore, the full-scale plants cannot be used as sources of treated, but not chlorinated or chloraminated, water. A pilot plant

owned and operated by the City of Austin was run to generate treated water. The pilot plant, located at the City of Austin's Robert C. Ullrich Water Treatment Plant, was supplied continuously with Lake Austin water from the plant's raw water intake. The water underwent softening, sedimentation, and filtration under conditions that simulated full-scale plant performance. Chemical additions included lime (100 mg/L as CaO) for softening and iron (3.5 mg/L) to aid in coagulation.

3.1.2.2 Coagulation

As with Lake Austin, Brick Utilities cannot be used as a source of treated Metedeconk River water because disinfectant is added prior to coagulation. Therefore, source water underwent batch alum coagulation, sedimentation, and filtration. Alum coagulation, performed 8 to 10 L at a time, simulated the conditions and coagulation procedure at Brick Utilities. Sodium bicarbonate was added to the source water prior to treatment to allow for a residual alkalinity between 40 and 50 mg/L as $CaCO_3$, and 55 mg/L of alum ($Al_2(SO_4)_3 \cdot 14\text{-}18\ H_2O$) was added for coagulation. The water was rapid mixed at 300 rpm for 30 seconds in a jar test apparatus, then slowly mixed at 50 rpm for 15 minutes, and finally settled for 75 minutes. Alum and sodium bicarbonate were added simultaneously during rapid mixing. The supernatant was filtered through 47-mm diameter, 0.7-µm nominal pore size GF/F glass-fiber filters, (Whatman® International Ltd, Maidstone, England) immediately after settling and stored at 4ºC for a maximum of one week before chloramination analyses. Both the alum coagulated and source waters were monitored for alkalinity, pH, UV, turbidity, and DOC.

3.1.2.3 Biodegradation

Natural organic matter in Metedeconk River source water was biodegraded at the University of New Hampshire using an adaptation of the "shaker-batch" method

originally developed by Wang and Summers (1995) and Allgeier *et al.* (1996). The biodegraded water was prepared by allowing the source water a 5-day contact time with natural bacteria attached to a sand media. The biofilter, which consisted of PVC columns packed with sand, was kept biologically active by continually recirculating Durham, NH source water in a constant temperature room at 20 °C. The Durham source served as the initial seed as well as the nutrient source. A fresh two-liter sample of Durham source water was obtained weekly to ensure an adequate supply of nutrients to the sand's biofilm. The sand columns were acclimated for three days with Metedeconk River source water prior to analysis. The acclimated sand was washed immediately before use with chlorine-free water until the UV absorbance of the rinse water was between 0.02 and 0.05 cm^{-1}. Then, each of several 500 mL-aliquots of the source water sample was combined with 150 g of acclimated washed sand in 1-L amber bottles, placed on an orbital shaker table at 120 rpm, and left in the dark at a constant temperature of 20ºC for five days. At the end of the incubation time, all the aliquots of water sample were combined to generate a biodegraded water fraction of 8 to 10 L. At time zero, two, and five days, small aliquots of water were analyzed for dissolved organic carbon (DOC). The biodegraded DOC was determined by the difference between the initial and the remaining DOC after the 5-day incubation period.

3.1.2.4 Apparent Molecular Weight and Distribution

Waters were fractionated using an ultrafiltration membrane (Amicon Corp., Danvers, MA) with a molecular weight (MW) cut-off of 3000 daltons (Collins *et al*., 1986). This molecular wight cut-off generated an adequate amount of water for subsequent analyes as well as separated the higher and lower molecular weight fractions, allowing the preferential removal of NOM through treatment processes to be investigated. Lower molecular weight cut-offs were not used because the waters were

also fractionated into hydrophilic and hydrophobic fractions via adsorption chromatography. YM/YC type membranes (62 mm diameter) were prepared as recommended by the manufacturer and verified to meet required flux ratings using a nitrogen pressurized, stirred container. Apparent molecular weight (AMW) quantification was made by measuring DOC and UV absorbance at 254 nm from the ultrafilter permeate. In addition to collection of the permeate, DOC and UV absorbance grab samples were collected and monitored with permeate volume to correct for concentration polarization at the membrane surface (Logan and Jiang, 1990). Batch filtration was performed to generate a water fraction of 7 to 9 L. AMW fractionation and analyses were performed at the University of New Hampshire.

3.1.2.5 NOM Hydrophibicity and Fractionation

Adsorption chromatography using XAD-8 and XAD-4 resins (Rohm and Haas, Co., Philadelphia, PA) was used to fractionate source water samples into hydrophobic, transphilic, and hydrophilic fractions (Malcolm 1991, Leenheer 1981, and Croué *et al*., 1993). Water samples were first fractionated into hydrophobic and trans/hydrophilic fractions using XAD-8 resin. The water sources were first filtered (0.7-µm GF/F, Whatman® International Ltd, Maidstone, England), acidified to pH 2, and then applied to the XAD-8 resin. The hydrophobic fraction of the TOC adsorbs to the XAD-8, while the transphilic and hydrophilic fractions pass through. Subsequent application of trans/hydrophilic fractions to the XAD-4 resin retained the transphilic fraction, while the hydrophilic fraction passed through. The hydrophobic and transphilic fractions were removed from the XAD-8 and XAD-4 resins, respectively, by eluting with 0.1 N NaOH. Periodic mass balances were performed on each resin to account for the entire sample TOC. Batch adsorption chromatography was performed using only XAD-8 resin to

generate a hydrophilic and hydrophobic water fraction of 7 to 9 L. NOM fractionation was performed at the University of New Hampshire.

3.1.3. Characterization

The waters studied were characterized by measuring the pH, alkalinity, UV_{254}, turbidity, and bromide concentration. The NOM in these waters was typically characterized by TOC, DOC, hydrophilic DOC, transphilic DOC, hydrophobic DOC, < 3K AMW, and > 3K AMW fractions. The DBPs were characterized by the uniform formation conditions (UFC) HAA_9 and softening uniform formation conditions (SUFC) HAA_9 tests. In addition, specific UV absorbance (SUVA), which is the ratio of UV_{254} and DOC, and Br^-/DOC ratios were calculated. Details of the analytical methods are presented in subsequent sections of this chapter.

3.2. BATCH SCREENING EXPERIMENTAL PROCEDURE

Two water sources of differing water quality were studied in the initial batch screening experiments. These experiments were conducted on Lake Austin, Texas water and Metedeconk River, New Jersey water. The selected waters were subjected to various treatments and NOM fractionations. The Lake Austin waters tested included "typical" source water, softened water, the hydrophilic fraction of the source water, and source water at summer algal levels. The Metedeconk River waters tested consisted of source, coagulated, < 3K AMW, and biodegraded waters, as well as the hydrophilic fraction of the source water. The hydrophobic fractions of both waters were not tested in the laboratory, but were determined by the difference between the source and hydrophilic fractions. Similarly, the > 3K AMW fraction of the Metedeconk River water was determined by the difference between the source and < 3K AMW fraction. The Lake Austin and Metedeconk River source waters, treated waters, and NOM fractions resulted

in the study of 12 different waters. These 12 waters were selected to both simulate the effect of treatment and to study the reactivity of specific NOM fractions.

The key objective of the batch screening experiments was to identify the water quality and chloramination variables that are most important in DXAA formation, which was achieved by testing a series of source waters, treated waters, and NOM fractions as outlined above. The screening approach used a fractional experimental design to systematically evaluate the many factors that might influence DBP formation during chloramination. Each water was exposed to sixteen separate experimental conditions that were used to evaluate the influence of Cl_2/N ratio, pH, temperature, chloramine residual concentration, and bromide concentration on DXAA formation. This experimental design allowed the evaluation of these factors by analysis of variance (ANOVA). A subsequent section of this chapter describes the use of ANOVA in more detail. Two levels of each of the five variables were selected for these experiments (Table 3-1). The levels of the experimental variables were chosen to be representative of current water treatment practices and to provide an adequate range between the two values of each variable for the purposes of observing effects. The resulting experimental design (Table 3-2) allowed the identification of the major water quality and chloramination variables that contribute to DXAA formation.

Table 3-1 – Chloramination and water quality variables evaluated in the initial batch screening experiments

Factor Levels	**Cl_2/N Ratio**	**pH**	**Temperature**	**Chloramine Residual**	**Bromide Concentration**
1	3/1	7	Ambient (~70°F)	2 mg/L	Ambient
2	5/1	9	85°F	4 mg/L	Ambient + 0.5 mg/L

Table 3-2 – Summary of experimental variables for fractional factorial batch tests

Trial No.	Experimental Variables				
	pH	Cl_2/N Mass Ratio	Temperature (°F)	Bromide Concentration (mg/L)	Chloramine Residual (mg/L as Cl_2)
1	7	3/1	70	Ambient	2
2	7	3/1	70	Ambient + 0.5	4
3	7	3/1	85	Ambient	4
4	7	3/1	85	Ambient + 0.5	2
5	7	5/1	70	Ambient	4
6	7	5/1	70	Ambient + 0.5	2
7	7	5/1	85	Ambient	2
8	7	5/1	85	Ambient + 0.5	4
9	9	5/1	70	Ambient	4
10	9	5/1	70	Ambient + 0.5	2
11	9	5/1	85	Ambient	2
12	9	5/1	85	Ambient + 0.5	4
13	9	3/1	70	Ambient	2
14	9	3/1	70	Ambient + 0.5	4
15	9	3/1	85	Ambient	4
16	9	3/1	85	Ambient + 0.5	2

Additional batch experiments were conducted to further study the most important variables identified from the fractional factorial batch tests, pH and Br^-/DOC ratio. The Br^-/DOC ratio was selected instead of bromide alone to normalize the DOC concentrations among the waters. Source and softened waters from Biscayne Aquifer, FL and St. Paul, MN were studied to broaden the range of water characteristics examined.

Samples were incubated in 250-mL brown, glass bottles capped with a Teflon-lined septa to simulate the formation of DBPs through a treatment plant and distribution system. Prior to dosing with chloramines, the water to be tested was brought to the

appropriate temperature and the pH was adjusted with nitric acid or sodium hydroxide. Strong acid or base was used, rather than a buffer, to eliminate any competing reactions. A sequential filling procedure was used in all the batch screening experiments to achieve mixing. First, the bottles were partially filled with sample water, then the appropriate dosing solutions (e.g., chloramines or bromide) were added to the bottles, which were then completely filled and capped head-space-free with Teflon-lined septa. The bottles were then incubated for 48 hours. A standard, 48-hour incubation period was used to match the conditions in the work of Symons *et al*. (1998), to allow the DXAA formation reactions to proceed further toward completion, and to account for the fact that maximum rather than average distribution system residence times may be of regulatory interest (Diehl, 2000). In many experiments, two or three bottles were set up for each experimental condition and dosed with different initial concentrations of chloramines to ensure that at least one bottle was within 10% of the target chloramine residual concentration at the end of the incubation period. Bromide was added using a potassium bromide solution, and chloramines were added in the form of preformed chloramines. At the end of the incubation period, the chloramine residual was measured, and replicate samples were taken for HAA analyses from the bottle meeting the target residual concentration.

Bottles used for sample treatment in the batch screening experiments were prepared by soaking overnight in detergent, rinsing four times with hot tap water, and twice with distilled water. The glassware was then soaked for 24 hours in a 10 - 20 mg/L chlorine solution. Finally, the glassware was rinsed four times with distilled water, then twice with distilled, deionized water produced on a Milli-Q filter apparatus, and baked at 140 °C overnight.

Reagent grade chemicals were used for all solutions, which were mixed with distilled, deionized water produced on a Milli-Q filter apparatus. Before use, this water was determined to be free of chlorine demand.

3.3. KINETIC EXPERIMENTS

3.3.1. Without Prechlorination

The experiments conducted to characterize the DXAA formation kinetics during traditional chloramination (simultaneous ammonia and chlorine addition) are summarized in Table 3-3. Samples were incubated in 250-mL brown glass bottles and capped with Teflon-lined septa to simulate the formation of DBPs through a treatment plant and distribution system. Prior to dosing with chloramines, the water to be tested was brought to the appropriate temperature and the pH was adjusted with nitric acid or sodium hydroxide. All bottles in each experiment received the same initial dose of chloramines. A Cl_2/N mass ratio of 4/1 was used in all experiments, and the dose was selected to provide a target residual concentration of 2 mg/L at 48 hours. At the end of the incubation period, the chloramine residual was measured, and replicate samples were taken for HAA analyses. DXAA measurements were made after incubation times of 5 minutes and 0.25, 0.5, 1, 4, 8, 24, 48, and 72 hours. The effects of pH, bromide concentration, and treatment on DXAA formation kinetics were examined. The focuses of the kinetic experiments for each water are described in Table 3-3. Ammonium chloride, the quenching agent recommended by USEPA Method 552.2 was determined to be ineffective at quenching the HAA formation reactions at early reaction periods during chloramination. Dechlorination with a stoichiometric amount of sodium thiosulfate was also investigated; however, this method proved difficult to control and had the potential

to de-halogenate the HAAs. Therefore, HAA samples were extracted immediately after collection to avoid possible artifacts associated with quenching agents and holding times.

Table 3-3 – Kinetic experiments without prechlorination

Water	pH	Bromide	Focus
Lake Austin source	7	Ambient	pH and
Lake Austin source	9	Ambient	Treatment
Lake Austin softened	9	Ambient	
Metedeconk River source	8	Ambient	Br^- and
Metedeconk River coagulated	8	Ambient	Treatment
Metedeconk River source	8	+0.5 mg/L	
Lake Austin softened	9	Ambient	High
Charleston filtered	8	Ambient	Temperature
Charleston source	8	Ambient	Treatment
Charleston filtered	8	Ambient	
Biscayne Aquifer source	9	Ambient	Treatment
Biscayne Aquifer settled	9	Ambient	

3.3.2. With Prechlorination

Experiments were also conducted to determine the effects of prechlorination on HAA formation kinetics (Table 3-4). The experimental procedure was modified because the four THMs were measured in addition to the nine haloacetic acids (HAA_9). The modification was necessary to minimize THM volatilization losses. The temperature and pH of the waters were adjusted by the same methodology used for the kinetic experiments without prechlorination. A 4.3-L amber glass bottle was filled with sample water, dosed with the appropriate concentration of chlorine dosing solution, and capped head space-free with a Teflon-lined septum. The water was incubated under these conditions for a portion of the prechlorination period prior to being transferred to a

stainless steel tank with a floating cover and a sampling valve. Replicate samples were taken in 125-mL amber glass bottles prior to the transfer of exactly 4-L to the stainless steel tank. These samples were incubated for the remainder of the specified prechlorination time (5 or 20 minutes) and subsequently analyzed for total chlorine residual, HAA_9 and THMs. The appropriate amount of an ammonium sulfate solution was then added to the tank after the specified prechlorination time to achieve a 4/1 Cl_2/N mass ratio. Samples were collected from the tank in 250-mL brown glass bottles. THMs were measured immediately after the period of free chlorination and again at 72 hours, and HAA_9 was measured after the period of prechlorination, as well as after 0.5, 1, 4, 8, 24, 48, and 72 hours. Ammonium chloride was used to quench the HAA samples in the prechlorination experiments because Singer *et al*. (2002) showed it to be effective for chlorinated samples. The initial chlorine dose was selected such that only ammonia had to be added after the period of free chlorination to achieve the target residual combined chlorine concentration of 2 mg/L at 48 hours.

Table 3-4 – Kinetic experiments with prechlorination

Water	**pH**	**Bromide**	**Lag Time**
Lake Austin source	9	Ambient	5 min
Lake Austin source	9	Ambient	20 min
Metedeconk River coagulated	8	Ambient	5 min
Metedeconk River coagulated	8	Ambient	20 min
Biscayne Aquifer settled	9	Ambient	5 min
Biscayne Aquifer settled	9	Ambient	20 min

3.4. SAMPLING OF DAVIS DRINKING WATER TREATMENT PLANT AND DISTRIBUTION SYSTEM

The Davis Drinking Water Treatment Plant and associated distribution system was sampled to confirm the HAA formation kinetics measured in the laboratory. This plant chlorinates Lake Austin source water for approximately 6 minutes prior to ammonia addition and softening. Duplicate samples were taken immediately before ammonia addition, after rapid mixing (ammonia and lime addition), after settling, and after filtration. The distribution system was also sampled at three different points that provided approximate residence times of 1.1, 2.4, and 3.1 days. The pH and chloramine residual concentration were measured at the time of sample collection. In addition, source and treated water was collected and characterized by measuring the pH, UV_{254}, DOC concentration, hydrophilic and hydrophobic DOC, and bromide concentration.

3.5. HALOAMINE REACTIVITY EXPERIMENTS

3.5.1. Bromamine Reactivity

The experiments conducted to characterize the reactivity of the bromamines in forming HAAs are summarized in Table 3-5. The natural waters were dosed with preformed bromamine stock solutions. Simultaneously, the concentrations of the individual bromamine species in the stock solutions were measured spectrophotometrically. The pH of the water matched that of the dosing solution to ensure that the bromamine speciation did not change upon dosing. The dose was selected to provide a target residual concentration between 0.5 and 1 mg/L as Cl_2 at 24 hours. Samples were incubated in brown glass bottles and capped headspace free with Teflon-lined septa. HAA_9 samples were taken at 5 minutes and again at 0.5, 1, 4, 24, 48, and 72 hours and extracted immediately to avoid complications that may arise due to sample preservation. Total combined oxidant concentrations were measured alongside the HAA

samples to determine total oxidant demand. To study the influence that natural waters may have on bromamine demand, control experiments were run with carbonate buffered Millipore water under the same experimental conditions as the bromamine reactivity experiments outlined in Table 3-5. The carbonate concentrations were added to match the concentration found in the natural waters. In addition, several controls were also run with chloramines instead of bromamines to determine relative differences in reactivity. These experiments were conducted at the same pH, buffer concentration, and initial haloamine dose as the bromamine reactivity experiments, but were dosed with preformed chloramines instead of bromamines.

Table 3-5 – Bromamine kinetic experiments

pH	Br^-/N molar ratio	Phosphate Buffer	Predominant Species
9	0.05	N	NH_2Br
9	0.05	Y	NH_2Br
7.2	0.05	Y	NH_2Br & $NHBr_2$
7.2	0.667	Y	$NHBr_2$

3.5.2. Bromochloramine Reactivity

Lake Austin source water was dosed with preformed bromochloramine stock solutions at pH 7.2 and 9 to mirror the conditions of the bromamine reactivity experiments. The pH of the dosing solution matched that of the water. Samples were incubated in brown glass bottles and capped headspace free with Teflon-lined septa. HAA_9 samples were taken at 5 min and again at 0.5, 1, 4, and 24 hours, and extracted immediately to avoid complications that may arise due to sample preservation. Total combined oxidant and monochloramine concentrations were measured immediately after dosing and alongside the HAA samples to determine total oxidant demand. In addition, haloamine speciation was monitored with membrane introduction mass spectrometry

(MIMS). To study the influence natural waters may have on bromochloramine demand, control experiments were run with carbonate buffered Millipore water under the same experimental conditions as the bromochloramine reactivity experiments. The carbonate concentrations were added to match the concentration found in the natural water. Since the bromochloramine stock solutions contained significant concentrations of monochloramine, several controls were run with monochloramine to determine relative differences in reactivity. These experiments were conducted at the same pH, buffer concentration, and initial chloramine dose as the bromochloramine reactivity experiments.

3.6. HALOAMINE SPECIATION EXPERIMENTS

The influences of pH, bromide concentration, and prechlorination were studied in 3 mM carbonate buffered high purity water (Table 3-6). The batch experiments were conducted in brown glass bottles and capped headspace free with Teflon-lined septa. The high purity, NOM free water was dosed with either 2 mg/L as Cl_2 preformed monochloramine or chlorine. In the prechlorination experiments, 0.5 mg/L as N ammonium sulfate was added after the 5 minute prechlorination period. Total combined oxidant and monochloramine concentrations were measured at 5 min and 1, 4, and 24 hours. In addition, the haloamine speciation was monitored by Membrane Introduction Mass Spectrometry (MIMS).

Table 3-6 – Haloamine speciation experiments

Disinfectant	pH	Bromide Concentration (mg/L)
Monochloramine*	9	0
Monochloramine*	9	0.5
Monochloramine*	7	0
Monochloramine*	7	0.5
5 min prechlorination**	9	0.5
5 min prechlorination**	7	0.5

* 4/1 Cl_2/N mass ratio

** 2 mg Cl_2/L HOCl followed by 0.5 mg N/L ammonia addition after 5 minutes

Water matrix - 3mM carbonate buffer in Ultra Pure Water (UPW)

3.7. PREFORMED CHLORAMINES

Preformed chloramines were created by mixing aqueous ammonium sulfate ($(NH_4)_2SO_4$) and sodium hypochlorite (NaOCl) solutions. These solutions were formulated so that approximately equal volumes of the two, when combined, produced the desired Cl_2/N ratio. Both solutions were adjusted to pH 9 with nitric acid and/or sodium hydroxide. The concentration of the chlorine solution was measured according to Standard Method 4500-Cl B (APHA, 1998) and by spectrophotometry using a molar absorptivity of 362 $M^{-1}cm^{-1}$ at λ_{max} of 292 nm for OCl^- (Furman and Margerum 1998) prior to creating preformed chloramines. The volume of ammonium solution added was adjusted to ensure the correct Cl_2/N ratio. The chlorine solution was added slowly to the ammonium solution with constant mixing in an ice bath at 1 °C. After 15 minutes of mixing, the concentration of the chloramine solution was measured using Standard

Method 4500-Cl B and by spectrophotometry using a molar absorptivity of 461 $M^{-1}cm^{-1}$ at λ_{max} of 243 nm for NH_2Cl (Kumar *et al.,* 1986) prior to dosing the samples. Two measurements were made. If these measurements differed by more than 0.1 mg/L a second pair was made. If the second pair of measurements differed by more than 0.1 mg/L the solution was discarded and remixed. An average of the two appropriate measurements was used in the calculations. All solutions were mixed with distilled, deionized water produced on a Milli-Q filter apparatus and were mixed immediately before use and discarded after use. This procedure was used successfully in previous chloramination research (Symons *et al*., 1998).

3.8. CHLORINE DOSING SOLUTION

Hypochlorite stock solution was prepared with 4% minimum available chlorine Aldrich reagent grade sodium hypochlorite. To determine the concentration of the NaOCl solution, 2 mL of NaOCl were diluted to 25 mL with distilled, deionized water, and the concentration was measured according to Standard Method 4500-Cl B. The 4% minimum available chlorine reagent grade NaOCl was then diluted to the desired concentration of 5 mg/mL, and its pH was adjusted to pH 9 with nitric acid and/or sodium hydroxide. The chlorine concentration was determined prior to use via Standard Method 4500-Cl B and by spectrophotometry using a molar absorptivity of 362 $M^{-1}cm^{-1}$ at λ_{max} of 292 nm for OCl^- (Furman and Margerum 1998). The solution was stored at 4 °C until its concentration dropped below 4 mg/mL.

3.9. BROMINE DOSING SOLUTION

Bromine dosing solutions were prepared according to Lei *et al*. (2004) by mixing equimolar concentrations of NaOCl and NaBr. The reaction was allowed to proceed for

3 days prior to use. The OBr^- concentration was measured by spectrometry using a molar absorptivity of 332 $M^{-1}cm^{-1}$ at λ_{max} of 329 nm for OBr^- (Troy and Margerum 1991).

3.10. BROMAMINE DOSING SOLUTIONS

Bromamine dosing solutions were prepared by reacting HOBr with $(NH_4)_2SO_4$ at different molar ratios and pH to promote formation of predominantly mono- or dibromamine. The buffer capacity of the ammonia solution was used to ensure the dosing solutions reached the desired pH. When the buffer capacity provided by the ammonia solution was exceeded, a phosphate buffer was used to ensure the mixture reached the pH desired. The concentrations of the individual bromamine species were measured by spectrometry using the methodologies of Lei *et al*. (2004). Because the spectra of the individual bromamine species overlap, they were monitored at 3 different wavelengths. The concentrations of bromamines were determined by using the molar absorptivities outlined in Table 3-7 and solving the resulting system of three linear expressions for total absorbance. In addition, total combined oxidant was determined by Hach DPD Total Chlorine powder pillows with Hach DPD Method 8021.

Table 3-7 – Molar absorptivities ($M^{-1}cm^{-1}$) of bromamines at selected wavelenghts

Compound	**λ = 232**	**λ = 258**	**λ = 278**
NH_2Br	82	273	425
$NHBr_2$	2000	884	714
NBr_3	3810*	5000*	1400**

All values from Lei *et al*. (2004) except * (Cromer *et al*., 1980) and **(Galal-Gorchev and Morris 1965)

3.11. BROMOCHLORAMINE DOSING SOLUTIONS

Bromochloramine dosing solutions were formed by reacting 1.4 mM NH_2Cl with 7.05 mM NaBr in a 10 mM Phosphate buffer at pH 7.2 and a 10 mM carbonate buffer at pH 6.3. The NH_2Cl solution was preformed as described above at a 5/1 Cl_2/N mass ratio. The NHBrCl dosing solution was monitored by spectrometry at wavelengths of 220 nm, 243 nm, and 320 nm according to Valentine (1986). Bromochloramine displays a strong absorption peak near 220nm and a weak peak near 320 nm (Trofe *et al*., 1980 and Valentine 1986), and both NH_2Cl and NHBrCl absorb at 243 nm (Valentine 1986), which is the absorption maxima of NH_2Cl (Kumar *et al*., 1986). However, the molar absorptivities of NHBrCl at these wavelengths were estimated by comparisons with $NHCl_2$ and $NHBr_2$, limiting their accuracy. Therefore, Membrane Introduction Mass Spectrometry (MIMS) was also used to monitor the NHBrCl dosing solutions. The resulting MIMS spectra indicated the dosing solutions contained predominantly bromochloramine and monochloramine. Therefore, total haloamine concentrations were determined by Hach DPD (N,N-diethyl-p-phenylenediamine) Total Chlorine Reagent Powder Pillows with Hach DPD Method 8021, and monochloramine concentrations were determined by Hach Monochlor F Reagent Powder Pillows according to Hach Method 10171. The difference between these two measurements was used to estimate the bromochloramine concentrations. Waters were dosed with the pH 6.3 and pH 7.2 dosing solutions exactly 10 minutes and 30 minutes after they were mixed, respectively.

3.12. DICHLORAMINE SOLUTIONS

Dichloramine solutions were prepared by rapidly lowering the pH of a 1.5 mM NH_2Cl (Cl_2/N molar ratio of 0.9) solution to pH 3.5-4 by addition of HCl (Gray *et al*., 1978 and Valentine *et al.,* 1986). The reaction mixtures were allowed to stand at least 4 hours and were used the day of preparation. The $NHCl_2$ concentration was measured by

spectrometry using a molar absorptivity of 274 $M^{-1}cm^{-1}$ at λ_{max} of 294 nm for $NHCl_2$ (Kumar *et al.,* 1986).

3.13. UNIFORM FORMATION CONDITIONS (UFC) AND SOFTENING UNIFORM FORMATION CONDITIONS (SUFC)

Both the Uniform Formation Conditions (UFC) and Softening Uniform Formation Conditions (SUFC) tests were used to characterize and compare the HAA_9 formation of the source and treated waters. The conditions of the UFC test (24 ± 1 hr incubation at 20 ± 1 °C and pH 8 ± 0.2 with a chlorine residual of 1 ± 0.4 mg/L) represent the average conditions in US distribution systems. The UFC tests were performed using the method described by Summers *et al.* (1996). The SUFC test was performed identically except that the pH of combined hypochlorite-buffer dosing solution and sample were adjusted to 9 instead of 8 (Ralls 1999).

3.14. ANALYTICAL METHODS

3.14.1. Total and Dissolved Organic Carbon

TOC was determined by UV-light promoted persulfate oxidation with infrared carbon dioxide detection using a Sievers® Model 800 TOC Analyzer with autosampler. The TOC concentrations were measured as NPOC (non-purgeable organic carbon), in which inorganic carbon was removed by acidification with ACS grade phosphoric acid and sparging with prepurified nitrogen (Merriam-Grave Industrial, Springvale, ME).

Dehydrated potassium hydrogen phthalate ($C_8H_5KO_4$) was used to prepare a concentrated stock (1000 mg C/L) for preparation of calibration standards in distilled deionized water. Concentrated KHP stock was acidified with 1 mL of phosphoric acid and refrigerated for reuse up to one month. A calibration curve was generated by analyzing standards prepared as 0.2, 1, 5, 8, and 10 mg C/L. Calibration standards were generally prepared fresh for each run; otherwise, they were stored at 4 °C for up to two

weeks. When reused, standards were checked and accepted only if within 10% of their original concentration. Samples were preserved with ACS grade phosphoric acid to pH 1-2, stored at 4 °C for up to two weeks, and equilibrated to room temperature prior to analyses.

DOC analysis was identical to TOC analysis except that the samples were filtered with GF/F glass-fiber filters, 47-mm diameter, 0.7-µm nominal pore size (Whatman® International Ltd, Maidstone, England). To minimize leaching of organic carbon into the sample, filters were first ignited at 500 ºC for one hour, then placed on a glass vacuum filtration apparatus (Kontes) and rinsed with 750 mL of distilled deionized water. One, 50 mL-aliquot of sample was filtered and discarded prior to filtrate collection.

Glassware for organic carbon analysis was washed with Alconox, rinsed three times with tap water and three times with distilled water and soaked in a 10% nitric acid bath for 2 hours. The glassware was then rinsed 3 times with distilled deionized water. Sample vials were baked at 550 °C for two hours, brown glass bottles were baked overnight at 400 °C, and volumetric glassware was rinsed with reagent grade acetone and allowed to air-dry.

3.14.2. Bromide

Bromide analyses were performed by the Brick Township Municipal Utilities Authority (Brick, NJ) by ion chromatography with conductivity detection in accordance with EPA Method 300.1. Samples were collected, ice-packed, and shipped overnight for analysis.

3.14.3. Residual Analysis

Glassware was prepared as described above in the batch screening experiments, except that glass was allowed to air-dry instead of being baked. All solutions were mixed with distilled, deionized water produced on a Milli-Q filter apparatus.

3.14.3.1 Total Chloramine Residual

Chloramine residual concentrations were measured by spectrophotometry as total chlorine using Hach DPD (N,N-diethyl-p-phenylenediamine) Total Chlorine Reagent Powder Pillows with Hach DPD Method 8021 adapted form Standard Method 4500-Cl. Initially, free chlorine was also measured with Hach DPD Free Chlorine Reagent Powder Pillows according to Hach DPD Method 8167, but under the typical drinking treatment conditions (neutral pH and Cl_2/N ratios of 3-5/1) virtually all of the chlorine is present as combined chlorine. Subsequently, free chlorine was not measured.

Standards of approximately 0, 1, 2, 3, 4, and 5 mg/L Cl_2 were analyzed in triplicate prior to sample analysis. The standards were created from the chlorine dosing solution described above. First, the exact concentration of the chlorine dosing solution was determined in accordance with Standard Method 4500-Cl B. Then, a primary dilution standard (PDS) was created by diluting the dosing solution to a concentration of 100 mg/L Cl_2 with distilled, deionized water. Finally, the standards were prepared by diluting the PDS to the desired concentration.

3.14.3.2 Monochloramine Residual

Monochloramine was measured by spectrometry at 655 nm using Hach Monochlor F Reagent Powder Pillows according to Hach Method 10171. Monochloramine standards of approximately 0.5, 1, 2, 3, and 4 mg/L as Cl_2 were analyzed in triplicate prior to sample analysis.

3.14.3.3 Total Combined Oxidant Residual

Total combined oxidant residual was measured by spectrophotometry as total chlorine using Hach DPD (N,N-diethyl-p-phenylenediamine) Total Chlorine Reagent Powder Pillows with Hach DPD Method 8021 as described above.

3.14.3.4 Bromamine Residual

The concentrations of the individual bromamine species were measured by spectrometry in a 10-cm pathlength quartz cell utilizing the methodologies of Lei *et al*. (2004) as described above.

3.14.4. Disinfection By-Product Analysis

3.14.4.1 Haloacetic Acids

The nine haloacetic acids (HAA_9) were measured by liquid-liquid extraction in accordance with USEPA Method 552.2 with modifications (Ralls 1999). Chlorinated samples were preserved with 4.5 mg of ammonium chloride, producing a concentration of 100 mg/L, and stored at 4 °C for up to two weeks. Prior to analysis, samples were equilibrated to room temperature and weighed. Fifteen mL of sample was removed, and the vial was reweighed, resulting in approximately a 30-mL aliquot with the exact mass determined by the difference in the vial weights. Chloraminated samples were extracted immediately to avoid complications associated with sample preservation. Three grams of copper sulfate, 12 g of sodium sulfate, 1.5 mL of concentrated sulfuric acid, and 3.0 mL of MTBE were then added to the vial. The vial was immediately capped and shaken briefly by hand, then stored on its side to prevent the salts from solidifying. Samples were then placed on a mechanical shaker for 30 minutes. The samples were then allowed to stand quiescently for several minutes to allow separation of the aqueous and organic layers. To convert the HAAs that partitioned into the organic phase to their methyl

esters, exactly 2 mL of the ether layer was transferred to a vial containing 2 mL of acidic methanol (10% H_2SO_4/methanol solution) and placed in a 50 °C bath for 3 hours. The vials were then allowed to cool to room temperature and the acidic extract was neutralized by a back extraction with 4 mL of a saturated sodium bicarbonate solution. After the phases separated, a pasteur pipette was used to transfer the extract from the top of the vial to a GC autosampler vial. Extracts were stored at -50°C for up to 7 days before analysis.

Glassware was washed with Alconox, rinsed three times with tap water and three times with distilled water, and soaked in a 10% nitric acid bath for 2 hours. The glassware was then rinsed 3 times with distilled deionized water. Sample vials were baked at 550°C for two hours, brown glass bottles were baked overnight at 400°C, and volumetric glassware was rinsed with reagent grade acetone and allowed to air-dry.

Gas chromatographic analysis was performed on a Hewlett Packard 6890A Gas Chromatograph with a micro electron capture device (μECD) equipped with an autosampler. A 30 meter J&W DB1701 capillary column was used with hydrogen carrier gas, constant velocity, and splitless injection. One μL of sample was injected, three injections per standard and two per sample. The initial oven temperature was 40°C for 2 minutes, followed by a 2.5 °C/minute temperature ramp to 65°C, followed by a 10°C/minute temperature ramp to 85°C, followed by a 20 °C/minute temperature ramp to 205°C. An injector temperature of 210°C, and a detector temperature of 290°C were used.

Aqueous standards were extracted and analyzed in the same manner as the samples to compensate for extraction efficiency. 1,2-dibromopropane was used as the internal standard. The ratio of the area of the peak of interest to the peak of the internal standard was used to quantify concentration.

Two, five-point standard curves were prepared for with every GC run to eliminate the effect of possible equipment operating condition variations. The nominal concentrations of the two standard curves ranged from 0-3 μg/L and 0-20 μg/L. When necessary, additional standard curves were run to ensure that the measured sample HAA concentrations fell within the concentrations of the standard curve. In addition, calibration check standards, duplicate samples, and blanks were analyzed at a frequency of 10% of the analytical load. The calibration check standards were analyzed to ensure that the instrument was still in calibration. Recoveries of the check standards fell between 70% and 130% for all the HAAs, ensuring that the preceding samples were valid.

HAA analyses were performed both at the University of Texas and at the Brick Township Municipal Utilities Authority (Brick, NJ). The Brick Utilities laboratory, which has been certified by the New Jersey Department of Environmental Protection for a variety of drinking water and wastewater analyses since 1975, measured HAAs in accordance with USEPA Method 552.2. Split sampling was performed periodically to confirm that both labs were achieving comparable results.

3.14.4.2 Trihalomethanes

THMs were analyzed according to USEPA Method 551.1. THM samples were dosed with 0.75 g of sample preservative (5 g Na_2HPO_4, 195 g KH_2PO_4, and 1.2 g NH_4Cl) and stored at 4 °C for up to 14 days. Glassware was prepared in accordance with the procedure developed for HAA analysis.

Gas chromatographic analysis was performed on a Hewlett Packard 5890A Gas Chromatograph with an electron capture device (ECD) equipped with an autosampler. A J&W DB-5 capillary column was used with a helium carrier gas, constant velocity, and splitless injection. One μL of sample was injected, three injections per standard and two

per sample. The initial oven temperature was 32 °C for 3.5 minutes, followed by a 20 °C/minute temperature ramp to 72 °C, which was held for 3.5 minutes.

Aqueous standards were extracted and analyzed in the same manner as the samples to compensate for extraction efficiency. TCA was used as the internal standard. The ratio of the area of the peak of interest to the peak of the internal standard was used to quantify concentration.

A five point standard curve was developed for every GC run. The standard curve nominal concentrations ranged from 0-100 µg/L. In addition, calibration check standards, duplicate samples, and blanks were analyzed at a frequency of 10% of the analytical load. The calibration check standards were analyzed to ensure that the instrument was still in calibration. According to USEPA Method 551.1, recoveries of the check standards must fall between 75% and 125% for all the THMs. Recoveries between 95% and 105% were obtained in this research.

3.14.5. Membrane Introduction Mass Spectrometry (MIMS)

The Membrane Introduction Mass Spectrometry (MIMS) technique used in this research was developed by Shang and Blatchley (1999). A Finnigan PolarisQ GC/MS Benchtop Ion Trap Mass Spectrometer equipped with an Xcalibur™ data system was modified to a MIMS configuration (Figure 3-1). A flow-through membrane cell was installed in place of a GC column. A Master Flex (model # 7524-50) peristaltic pump with an Ismatec 8-roller pump head was used to transport analytes through the membrane cell. The membrane cell (Figure 3-2) was constructed with a ¼-inch o.d., 5-cm long glass tube with two ¼-inch stainless steel Swagelock T-joints. The membrane, 0.64-mm i.d., 1.19-mm o.d., 60-mm long silicone tubing (Dow Corning), was connected with 1/16-inch Teflon PFA tubing (Cole Parmer) and placed in the center of the membrane cell. Helium carrier gas was transported to the membrane cell via 0.1-mm i.d. deactivated

fused silica tubing (Agilent), and permeates were transferred with the carrier gas to the ion source via 0.53-mm i.d. deactivated fused silica tubing (Agilent). The membrane temperature was maintained at 60 °C by the GC oven, and the liquid flow (1 mL/min) was operated counter-currently to the helium flow (1 mL/min). The mass spectrometer was operated under 70 eV electron impact ionization (EI) conditions. The source temperature and transfer lines were maintained at 200°C. Mass spectra scan mode (45-270 amu) was used to evaluate haloamine speciation as well as for quantification of specific compounds.

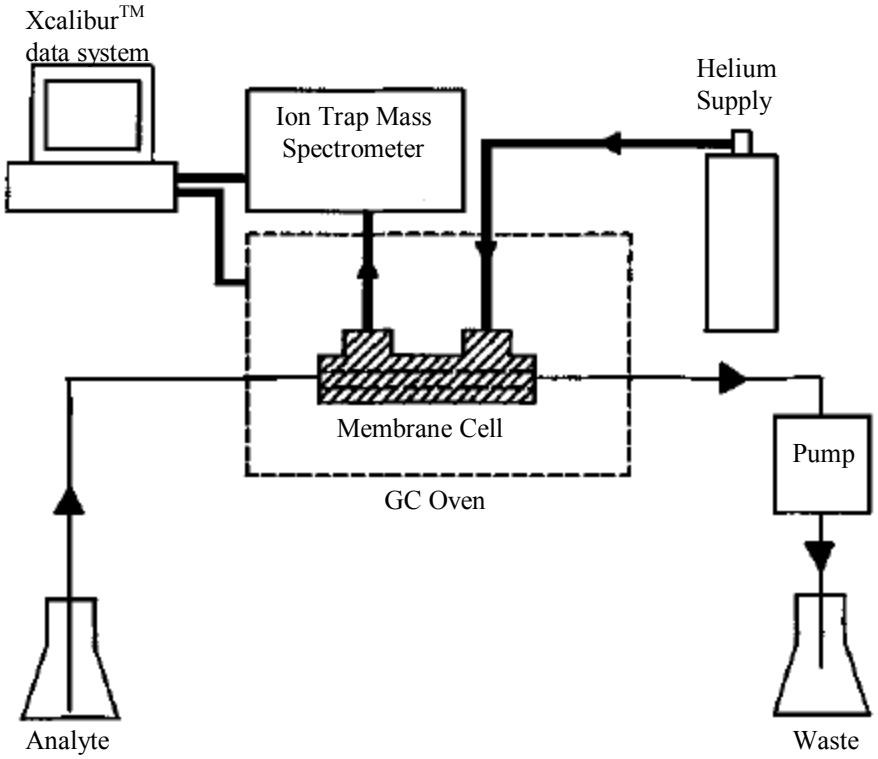


Figure 3-1 – MIMS system schematic (adapted from Shang and Blatchley 1999)

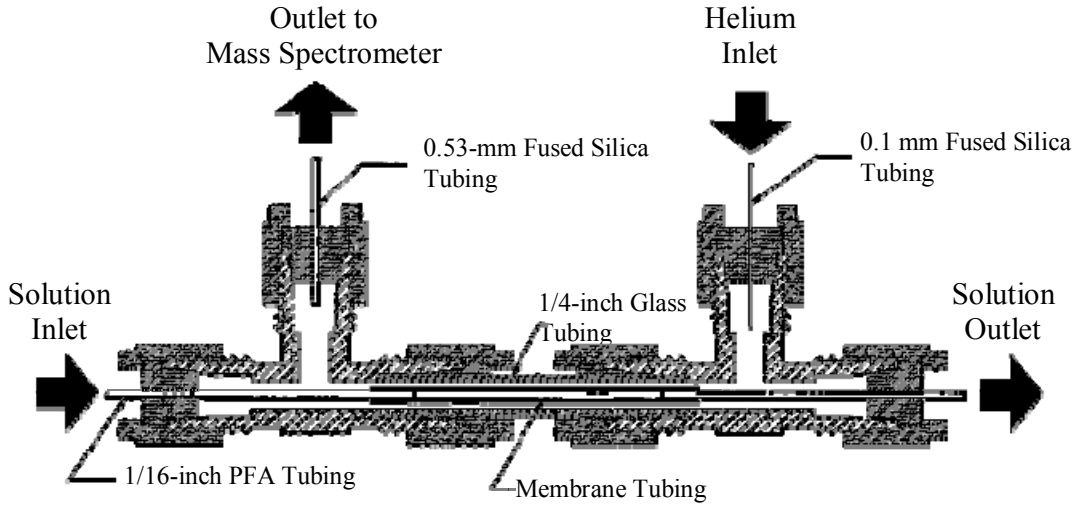


Figure 3-2 – Membrane cell (adapted from Shang and Blatchley 1999)

MIMS was used to detect the presence of chloro- and bromo-substituted haloamines as well as to track the kinetics of their formation and decay. Ultra pure water was pumped through the system until a stable background was reached. Once a stable background was obtained, haloamine standards were continuously introduced to the system in a step-wise manner to establish calibration curves. Each standard was pumped through the system until a steady-state abundance of the selected ions was obtained. Samples of unknown concentration were then introduced in the same manner as the standard solutions.

3.14.5.1 Chloramines

Chloramine compounds were determined by the methodology developed by Shang and Blatchley (1999). Ions with m/z values of 53 ($NH_2{}^{37}Cl^{\cdot+}$) and 87 ($NH^{35}Cl^{37}Cl^{\cdot+}$) were selected to monitor mono- and dichloramine, respectively. Mass spectra for mono- and dichloramine are shown in Figure 3-3. Monochloramine yielded large abundances at m/z 51 ($NH_2{}^{35}Cl^{\cdot+}$) and 53 ($NH_2{}^{37}Cl^{\cdot+}$). Dichloramine yielded large

abundances at m/z 85 ($NH^{35}Cl^{35}Cl^{\cdot+}$), 87($NH^{35}Cl^{37}Cl^{\cdot+}$), and 89($NH^{37}Cl^{37}Cl^{\cdot+}$), as well as at m/z 49 ($N^{35}Cl^{\cdot+}$), 51 ($N^{37}Cl^{\cdot+}$) which represent potential fragments of dichloramine. In addition to these fragments ions with m/z of 53 ($NH_2{}^{37}Cl^{\cdot+}$) were also observed. This may be due to unavoidable equilibria of the chloramines or may be due to the ionization conditions. However, the abundance of the m/z 53 ion is greater than can be attributed to chloramine equilibria. Besides analytes of interest, water can also diffuse across the membrane and has been used as an ioniziation gas in MIMS systems (Lauritsen *et al*., 1992; Wong and Cooks 1995). Therefore, fragments of dichloramine may protonate forming ions with m/z 53. These spectra agreed well with those obtained by Shang and Blatchely (1999). Therefore, m/z 87 was selected to quantify dichloramine, and m/z 53 was selected to quantify monochloramine. These ions were selected to minimize interferences from other inorganic chloramines and to be consistent with previous work. Because dichloramine also yielded ions at m/z 53, its contribution must be subtracted when quantifying monochloramine in the presence of dichloramine.

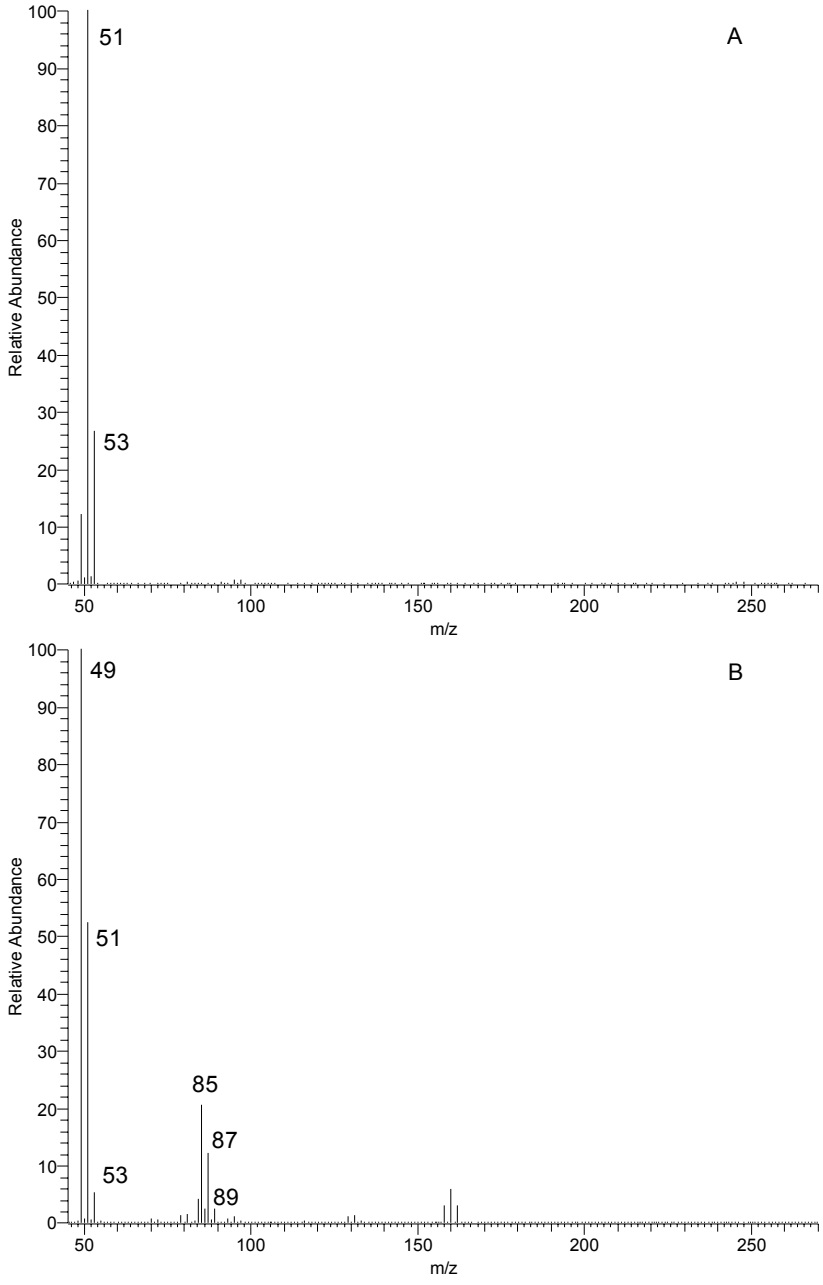


Figure 3-3 – Mass spectra obtained by MIMS for 5 mg Cl_2/L monochloramine (A) and 5 mg Cl_2/L dichloramine (B)

3.14.5.2 Bromamines

Mono- and dibromamine were identified and quantified by MIMS. Predominantly mono-and dibromamine solutions were prepared as described previously. Solutions were prepared at a pH of 7.2 and a Br_2/N molar ratio of 0.667 to form predominantly dibromamine and at a pH of 9 and a Br_2/N molar ratio of 0.05 to form predominantly monobromamine. Concentrations of these solutions were determined by spectrometry in a 10-cm pathlength quartz cell using the methodologies of Lei at al. (2004) as previously described, as well as by HACH DPD Method 8021. These measurements indicated that the monobromamine solutions contained small amounts of dibromamine; however, no monobromamine was measured by spectrometry in the dibromamine solution. Mass spectra for mono- and dibromamine are shown in Figure 3-4. Ions with m/z values of 95 ($NH_2{}^{79}Br^{\cdot+}$) and 97 ($NH_2{}^{81}Br^{\cdot+}$) represent monobromamine and m/z values of 173 ($NH^{79}Br^{79}Br^{\cdot+}$), 175 ($NH^{79}Br^{81}Br^{\cdot+}$), and 177 ($NH^{81}Br^{81}Br^{\cdot+}$) represent dibromamine. The isotopic patterns of the ions described above agreed with those calculated from natural abundances. In addition, ions at m/z 79 ($^{79}Br^{+}$), 81 ($^{81}Br^{+}$), 158 ($^{79}Br\ ^{79}Br^{+}$), 160 ($^{79}Br\ ^{81}Br^{+}$), and 162 ($^{81}Br\ ^{81}Br^{+}$) were also present. Potential fragments of both monobromamine and dibromamine include ions at m/z 93 ($NH^{79}Br^{\cdot+}$) and 95 ($NH^{81}Br^{\cdot+}$). Therefore, the ion m/z 97 was selected to quantify monobromamine. The ion m/z 177 was selected to quantify dibromamine to avoid interferences from bromoform, a common DBP, which produces ions at m/z 173 and 175. However, dibromamine also yielded ions at m/z 97; therefore, when quantifying monobromamine in the presence of dibromamine, its contribution must be subtracted.

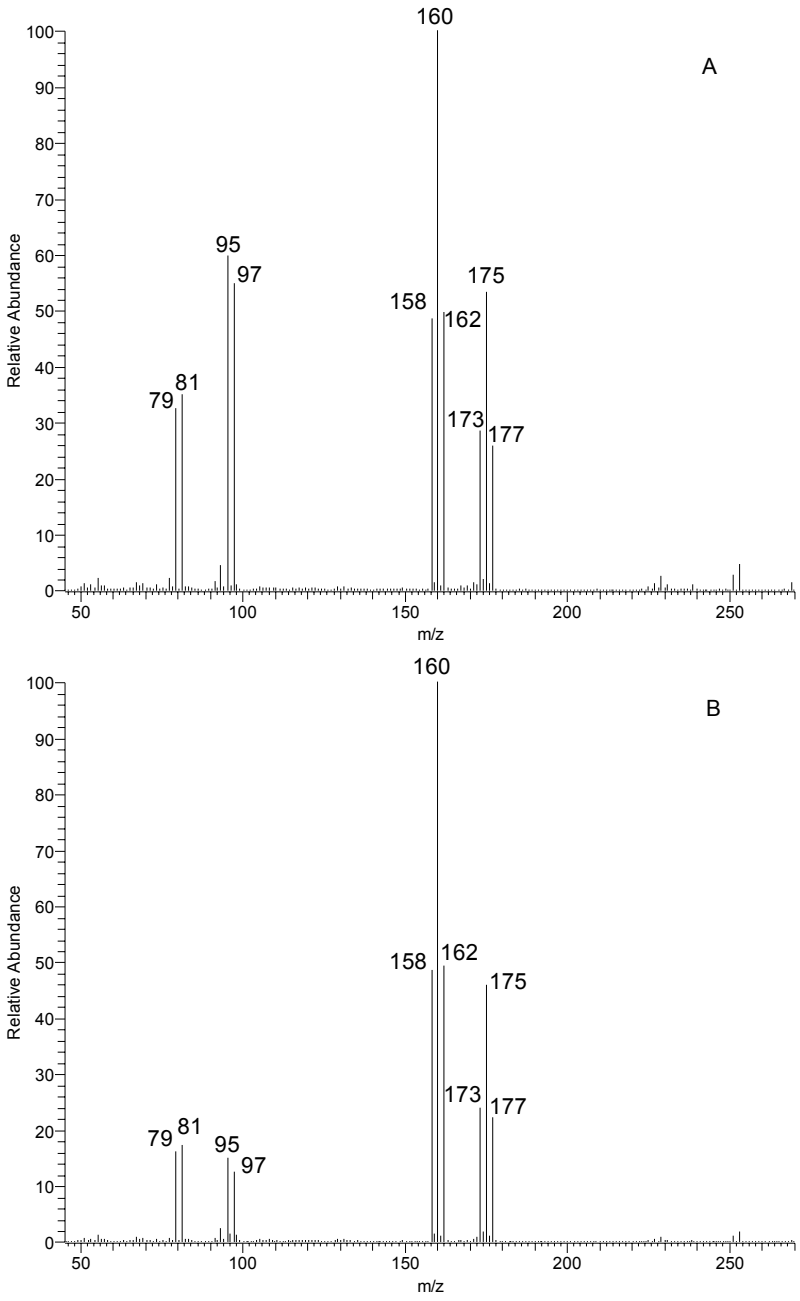


Figure 3-4 – Mass spectra obtained by MIMS for 5 mg Cl_2/L monobromamine (A) and 5 mg Cl_2/L dibromamine (B)

3.14.5.3 Bromochloramine

Gazda *et al*. (1993) formed NHBrCl by reacting NH_2Cl with Br^- at a 12:1 Br^-:NH_2Cl molar ratio and a pH of 6.5. These researchers monitored this reaction in real-time using MIMS and concluded that bromochloramine was the predominate reaction product. These reaction conditions resulted in rapid formation and decay of bromochloramine. Therefore, a lower Br^-:NH_2Cl molar ratio of 5:1 was used to slow the kinetics of bromochloramine decay. The resulting spectra of this reaction mixture is shown in Figure 3-5. The spectrum agreed well with that obtained by Gazda and Margerum (1993). Ions with m/z values of 51 ($NH_2{}^{35}Cl^{\cdot+}$) and 53 ($NH_2{}^{37}Cl^{\cdot+}$) represent monochloramine, and those with values of 129 ($NH^{79}Br^{35}Cl^{\cdot+}$), 131 ($NH^{79}Br^{37}Cl^{\cdot+}$ and $NH^{81}Br^{35}Cl^{\cdot+}$) and 133 ($NH^{81}Br^{37}Cl^{\cdot+}$) represent bromochloramine. In addition, ion fragments of bromochloramine observed at 79 ($^{79}Br^+$), 81 ($^{81}Br^+$), 93 ($NH^{79}Br^{\cdot+}$), and 95 ($NH^{81}Br^{\cdot+}$) were similar to those of Gazda and Margerum (1993). However, ions at m/z 97 ($NH_2{}^{81}Br^{\cdot+}$), 158 ($^{79}Br\ {}^{79}Br^+$), 160 ($^{79}Br\ {}^{81}Br^+$), and 162 ($^{81}Br\ {}^{81}Br^+$) were also observed. Monobromamine also produced ions at m/z 97; therefore, monobromamine may be present in the dosing solution. However, it is unlikely that significant quantities of monobromamine would be present at pH 6.3 (Lei *et al*., 2004); therefore, it may be a fragment of chorobromamine. Gazda and Margerum (1993) observed ions at m/z 97, but did not report observing the formation of ions clustered around m/z 160 (Br_2). These differences may be due to the MIMS configurations employed, Gazda and Margerum used a direct insertion membrane probe, whereas this research used a membrane cell. The ion m/z 131 ($NH^{79}Br^{37}Cl^{\cdot+}$ and $NH^{81}Br^{35}Cl^{\cdot+}$) was the most abundant ion that was unique to bromochloramine. Therefore, it was chosen to quantify bromochloramine.

Because NH_2Cl reacts with bromide to form NHBrCl, the NH_2Cl concentration decreased after bromide was added. However, the abundance observed at m/z 53 (the ion

chosen to monitor NH_2Cl) increased after bromide addition (Figure 3-6). Therefore, an ion at m/z 53 is probably a fragment of the NHClBr formed, potentially $NH^{37}Cl^{\cdot+}$ (m/z 52) that has been protonated, resulting in $NH_2{}^{37}Cl^{\cdot+}$. Therefore, NH_2Cl quantification is hindered by the presence of NHBrCl. However, monochloramine and total oxidant concentrations may be determined by Hach method 10171 and 8021, respectively. These concentrations in conjunction with the MIMS spectra of the individual haloamines allowed the quantification of the haloamines of interest.

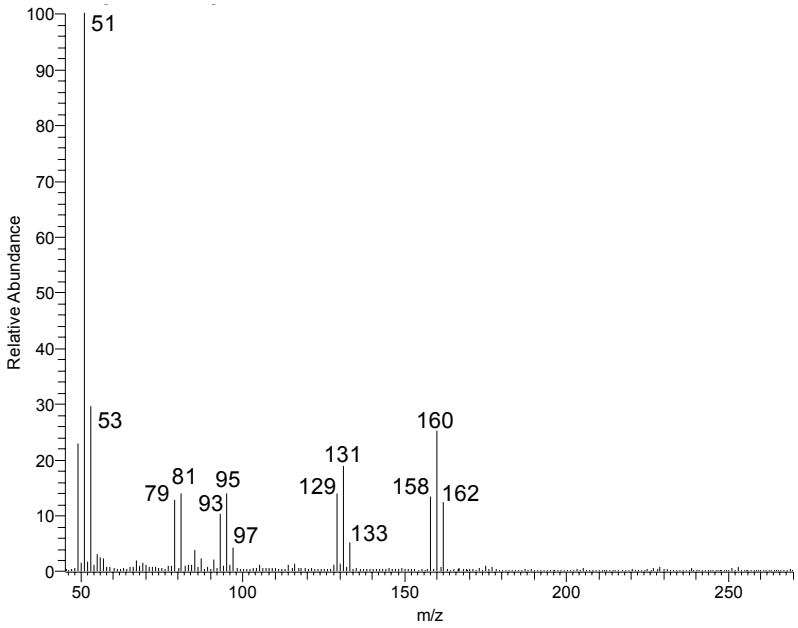


Figure 3-5 – Mass spectrum for 0.14 mM NH_2Cl + 0.7 mM Br^- (pH 6.3 and 5 mM Carbonate buffer) 10 minutes after Br^- addition

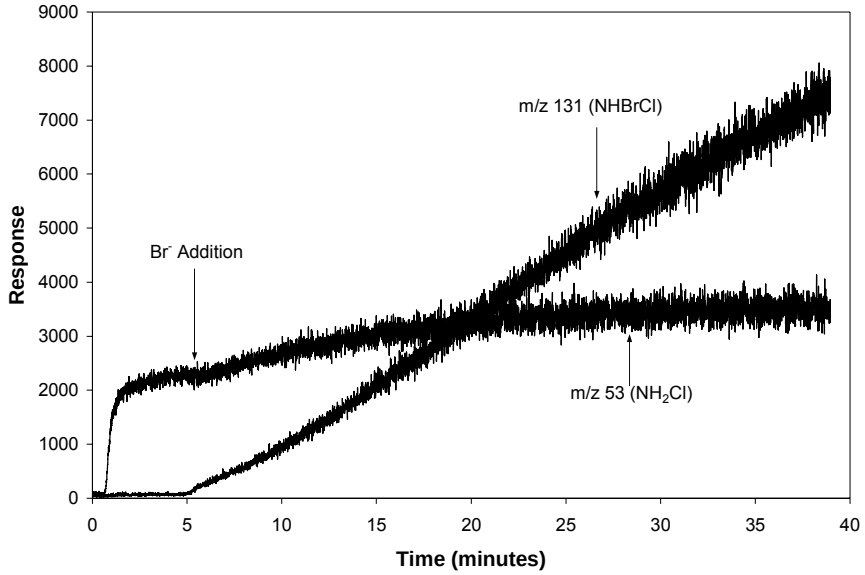


Figure 3-6 – Ion abundances of $NH^{79}Br^{37}Cl^{+}$ and $NH^{81}Br^{35}Cl^{+}$ (131) and $NH_2{}^{37}Cl^{+}$ (53) during on-line monitoring of the reaction of 0.14 mM NH_2Cl + 0.7 mM Br^- at pH 6.3 in 5 mM Carbonate buffer (NH_2Cl solution introduced at T = 0; Br^- added to solution at T = 5 min)

3.14.5.4 MIMS Calibration

Chloramine calibration curves were obtained by serial dilution of predominantly monochloramine and dichloramine solutions. These solutions were introduced to the MIMS system in a stepwise manner, and standard curves were developed based on the average steady-state abundance of selected ions. The monochloramine standard curve (m/z 53) and the dichloramine standard curve (m/z 87) are shown in Figure 3-7 and Figure 3-8, respectively. However, because dichloramine also produced ions at m/z 53, when determining monochloramine in the presence of dichloramine, the dichloramine contribution to the total m/z 53 abundance observed was subtracted with another standard curve (Figure 3-9). Under the conditions of this research, dichloramine concentrations were either not detected or very low, resulting in no or very slight contribution to the

signal at m/z 53. The limits of detection for mono- and dichloramine, based on a signal-to-noise ratio of 2, were 0.25 and 0.2 mg/L as Cl_2, respectively.

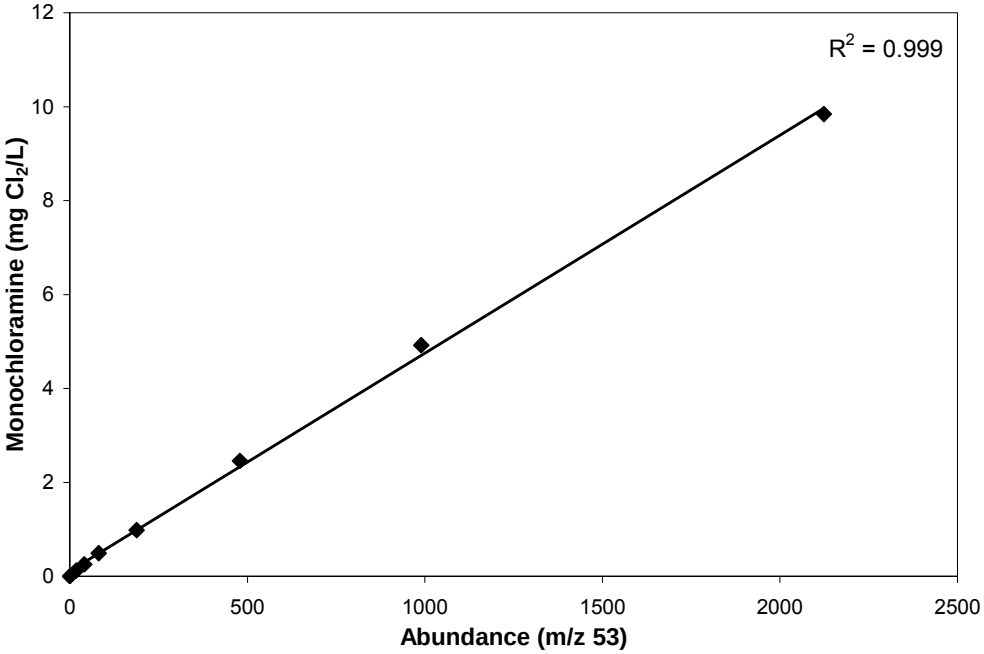


Figure 3-7 – Monochloramine standard curve (m/z 53)

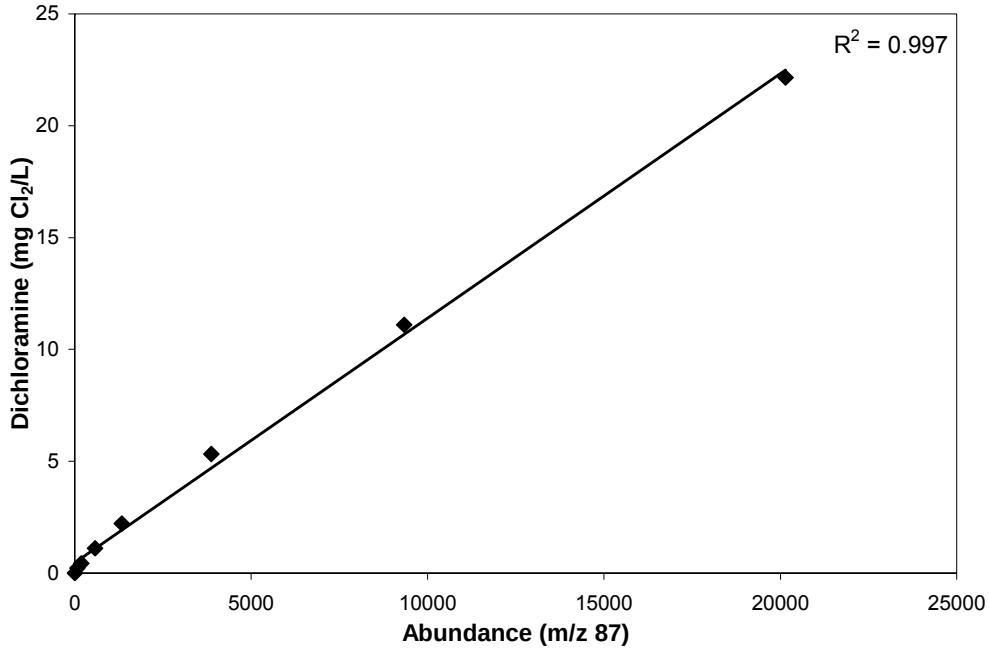


Figure 3-8 – Dichloramine standard curve (m/z 87)

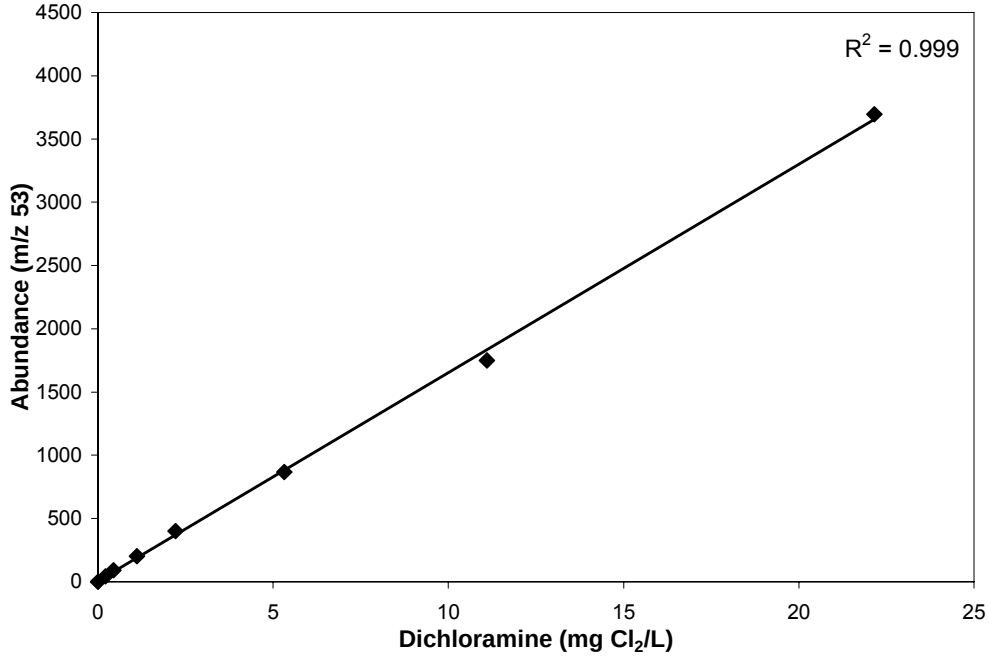


Figure 3-9 – Dichloramine contribution to m/z 53 standard curve

Dibromamine solutions were relatively unstable and decayed too rapidly to develop calibration curves by serial dilution of a stock solution. Therefore, as the dibromamine solution decayed, it was monitored by MIMS for several hours until no dibromamine was detected. Bromamine concentrations were measured simultaneously by spectroscopy as previously described. The dibromamine standard curve (m/z 177) developed is shown in Figure 3-10. No monobromamine was detected in the dibromamine solutions by spectroscopy. Therefore, the ions measured at m/z 97 were assumed to be fragments of dibromamine. Monobromamine calibration curves were developed by serial dilution of a predominantly monobromamine solution. These solutions were introduced to the MIMS system in a stepwise manner and their concentrations were checked by spectroscopy as previously described. However, the monobromamine solution contained small concentrations of dibromamine; therefore, its contribution to the total m/z 97 abundance (Figure 3-11) was subtracted to obtain the monobromamine standard curve (Figure 3-12). Under the conditions of this research, dibromamine concentrations were present in concentrations that resulted in significant contribution to the signal at m/z 97. However, even after correction for dibromamine interference, relatively good R^2 values were still obtained. The limits of detection for mono- and dibromamine, based on a signal-to-noise ratio of 2, were 0.35 and 0.15 mg/L as Cl_2, respectively.

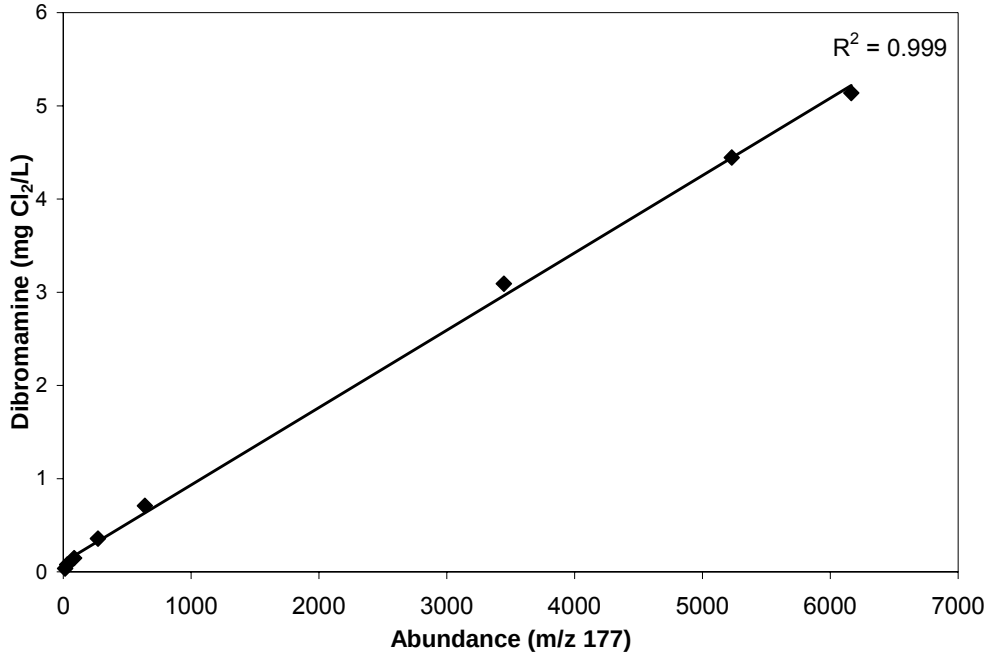


Figure 3-10 – Dibromamine standard curve (m/z 177)

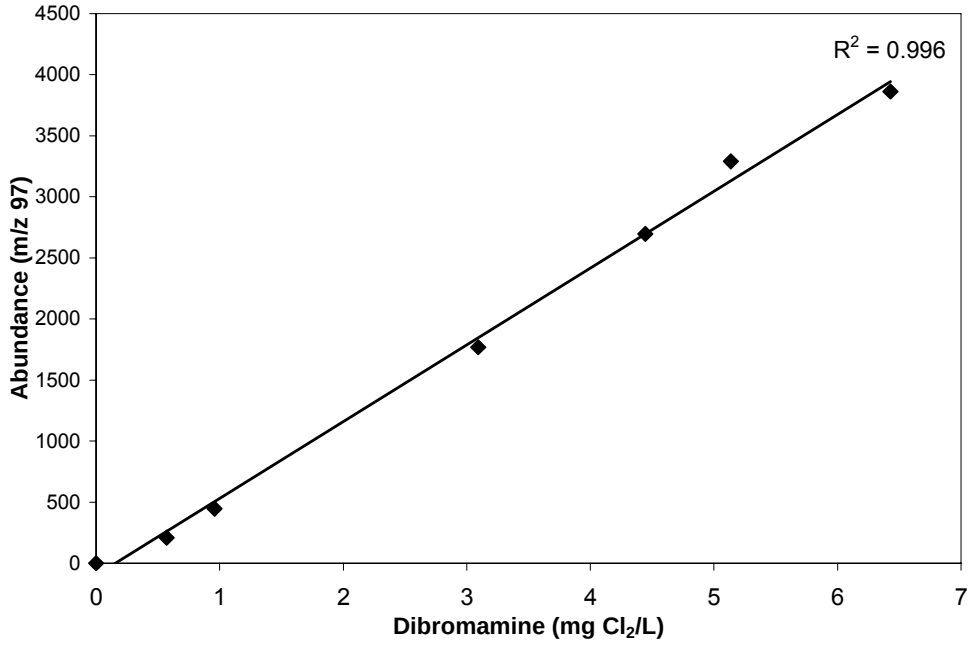


Figure 3-11 – Dibromamine contribution to m/z 97 standard curve

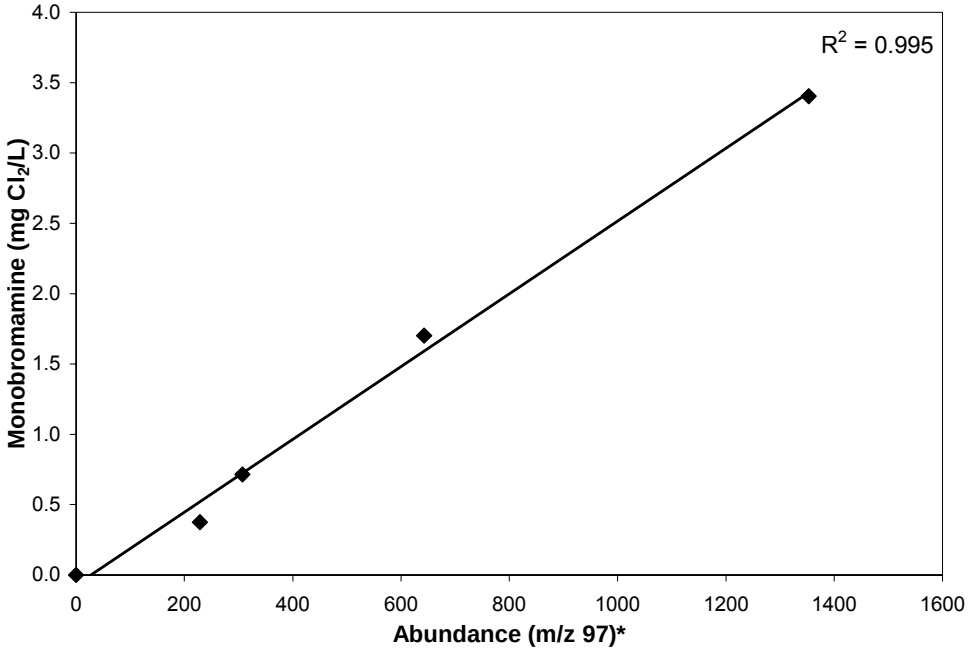


Figure 3-12 – Monobromamine standard curve (m/z 97) *Dibromamine interference subtracted

Bromochloramine calibration curves were developed by monitoring 1:10 dilutions of the bromochloramine dosing solutions. These solutions were also unstable; therefore, they were periodically introduced to the MIMS system for several hours. The total haloamine concentration, determined by Hach Method 8021, and the monochloramine concentration, determined by Hach Method 10171, were measured simultaneously. The bromochloramine dosing solutions contained predominantly monochloramine and bromochloramine, with trace amounts of dibromamine. Therefore, the bromochloramine concentration was determined by the total haloamine concentration, less the monochloramine concentration, less the dibromamine concentration, measured by MIMS at m/z 177. The resulting bromochloramine standard curve (m/z 131) is shown in Figure 3-13.

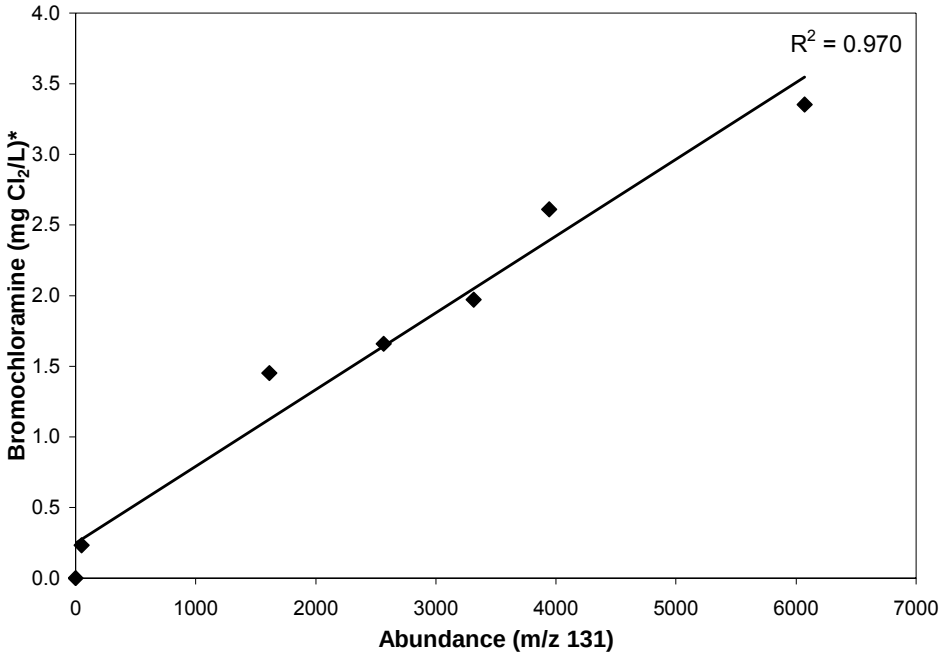


Figure 3-13 – Bromochloramine standard curve (m/z 131) *Bromochloramine concentration determined by the difference between the total haloamine (Hach DPD Total Chlorine reagent) and the monochloramine (Hach Monochlor-F reagent) less the dibromamine concentration present (MIMS m/z 177)

Bromochloramine also produced ions at m/z 53; therefore, standard curves were developed to remove its contribution to these ions to permit determination of monochloramine and monobromamine concentrations by MIMS in the presence of bromochloramine. As noted above, the bromochloramine standard solutions also contained monochloramine. The, monochloramine concentrations in the standards were determined by Hach Method 10171, and the contribution of monochloramine to m/z 53 was determined using the standard curve in Figure 3-14. The monochloramine contribution was subtracted from the total abundance resulting in the bromochloramine contribution to the m/z 53 abundance (Figure 3-15). A comparison of Figures 3-14 and 3-15 shows that, when present, bromochloramine significantly contributes to the m/z 53 signal.

In a similar fashion, the contribution of NHBrCl to m/z 97 was characterized to permit MIMS quantification of monobromamine in the presence of bromochloramine. A more linear response was observed when the ion at m/z 97 was assumed to be a fragment of bromochloramine, and not monobromamine (Figure 3-16). Therefore, the ion abundance observed at m/z 97 is most likely due to fragments of bromochloramine and dibromamine, not monobromamine. The bromochloramine contribution to m/z 97 (Figure 3-17) was determined by subtracting the contribution of dibromamine from the total amount of m/z 97 ion present. The R^2 values for the bromochloramine standard curves were not as good as those obtained for the chloramines or bromamines. However, significantly more error is introduced when quantifying bromochloramine because of the overlapping spectra of this compound with chloramines and bromamine species also present. The limit of detection for bromochloramine, based on a signal-to-noise ratio of 2, was 0.4 mg/L as Cl_2.

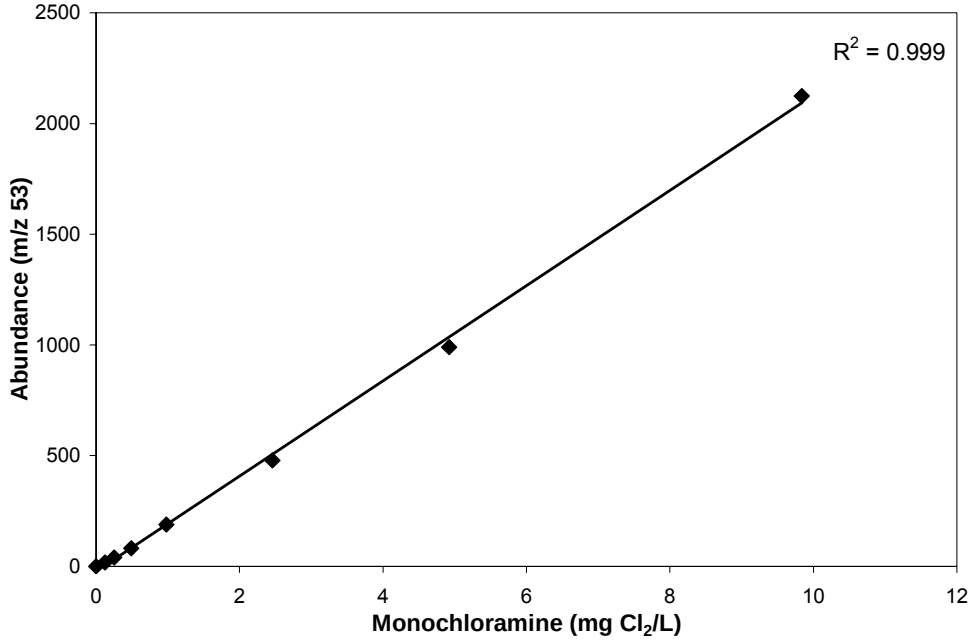


Figure 3-14 – Monochloramine contribution to m/z 53 standard curve

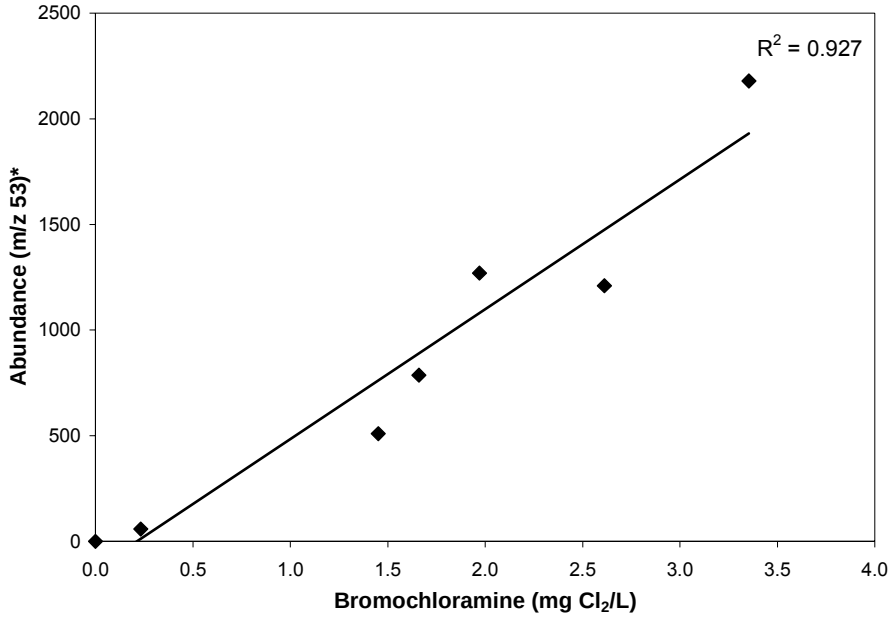


Figure 3-15 – Bromochloramine contribution to m/z 53 standard curve *total abundance less the abundance due to monochloramine

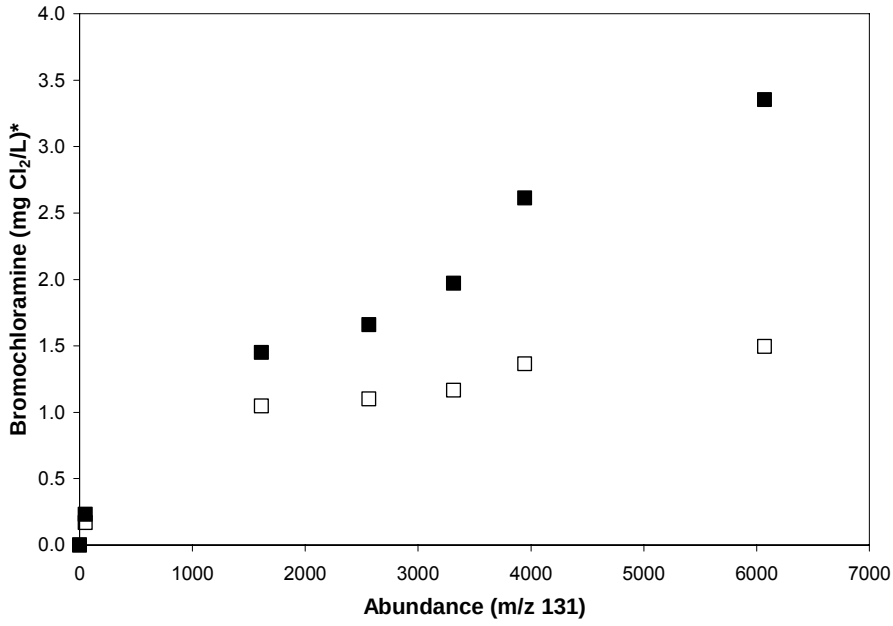


Figure 3-16 – Bromochloramine calibration (solid symbols represent NHBrCl concentration assuming no NH_2Br present, open symbols represent NHBrCl concentration assuming NH_2Br present)

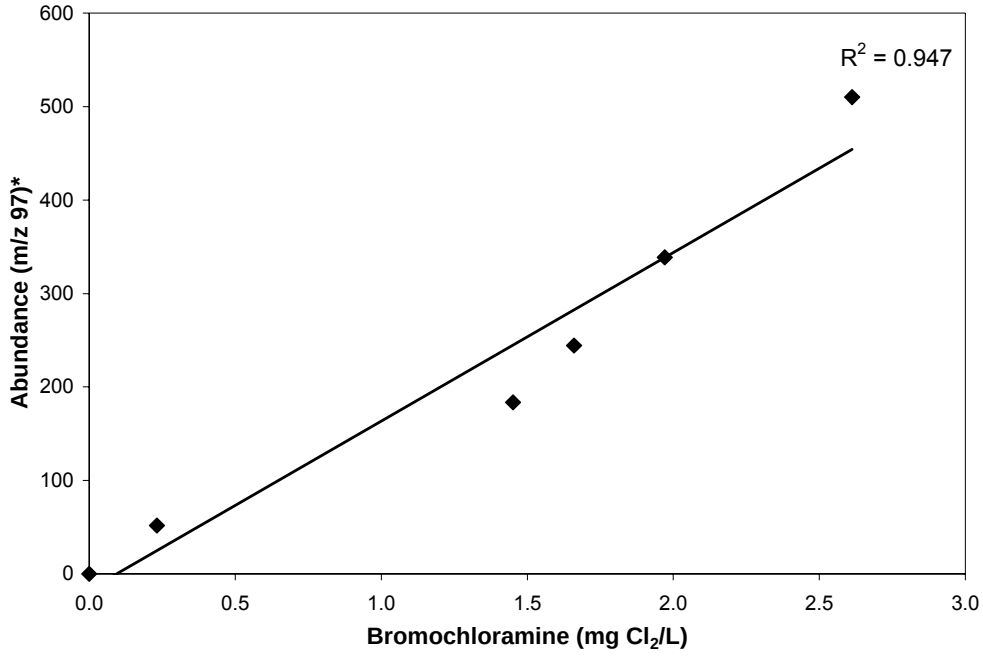


Figure 3-17 - Bromochloramine contribution to m/z 97 standard curve *total abundance less the abundance from dibromamine

3.14.6. Other Analytical Methods

Alkalinity was measured following Standard Method 2320 (APHA, 1998), turbidity was measured using Standard Method 2130 (APHA, 1998), the pH of various solutions and samples was determined using Standard Method 4500 H^+ (APHA, 1998), and the ultra-violet light absorbance was measured at 253.7 nm in accordance with Standard Method 5910 (APHA, 1998).

3.15. ANALYSIS OF VARIANCE (ANOVA)

In the batch screening experiments, each water was exposed to sixteen separate experimental conditions that were used to evaluate the influence of Cl_2/N ratio, pH, temperature, chloramine residual concentration, and bromide concentration on DXAA formation. This experimental design allowed the evaluation of these factors using

analysis of variance (ANOVA) without confounding (Ross 1988). Two levels of each of the five variables were selected for these experiments (Table 3-1). The levels of the experimental variables were chosen to be representative of current water treatment practices and to provide an adequate range between the two variables for the purposes of observing effects. The resulting 16-trial experimental design (Table 3-2) allows the identification of the major water quality and chloramination variables that contribute to DXAA formation. This design also allowed various combinations of the different waters studied to be incorporated into the ANOVA analysis as a sixth variable, water source/treatment. An F-test was performed to determine the significance of each variable at various levels of confidence. Variables were considered to be significant if they exceeded a confidence level of 90%; however, a majority (greater than 70%) of the variables was within a 99% confidence level. Variables below the 90% confidence level were included in an error term. The significant variables were then ranked to determine the relative effect of each according to their percent contribution to the total variation of the DXAA formation data. Example ANOVA calculations are provided in Appendix A.

3.16. MODELING

A unified haloamine kinetic model was developed to aid in understanding the complexity of haloamine chemistry. The model is a compilation of the monochloramine autodecomposition model developed by Jafvert and Valentine (1992) and Vikesland *et al*. (2001), the bromamine decomposition model developed by Lei *et al*. (2004), bromochloramine formation reactions (Trofe *et al.,* 1980 and Gazda and Margerum 1994), as well as various HOBr (Kumar and Margerum 1987) and NH_2Br (Wajon and Morris 1980) formation reactions. The model consists of a system of ordinary differential equations for the rate expressions and algebraic expressions for the equilibrium expressions that describe the reactive system. Ionic strength effects for all

equilibria were considered using the extended DeBye-Huckel relationship to calculate activity coefficients. In addition, the model allowed pH to vary or be fixed by using appropriate buffer intensity relationships according to the presumed reaction stoichiometry. When available from the literature, temperature dependencies were also incorporated into the model. Model results were obtained by solving the equations using the software package *Scientist* (1995), which uses Gear's Method to solve simultaneous differential equations. A literature search was conducted to determine the significance of reactions as well as their corresponding rate constants. If rate constants were not available in the literature, the model was used to estimate them using non-linear regression analysis techniques. *Scientist* (1995) uses a modified Powell algorithm to minimize the unweighted sum of the squares of the residual error between the predicted and experimentally observed values to estimate specific parameters in the model. Upper and lower bounds were placed on each parameter to be estimated so as not to exceed reasonable estimates.

CHAPTER 4: Relative Significance of Factors Influencing DXAA Formation during Chloramination

4.1. INTRODUCTION

Several variables influence HAA formation, such as natural organic matter (NOM) characteristics, pH, Cl_2/N ratio, disinfectant residual concentration, and bromide ion concentration. Although each of the aforementioned variables has been previously studied, the relative importance of each of these variables in contributing to DXAA formation during chloramination has not been elucidated. This research was designed to look more comprehensively and in a statistically rigorous fashion at the relative importance of these many factors in contributing to DXAA formation through a multi-factor, two-level, factorial experimental design. In addition, further study into the reactivity of NOM fractions as well as the impact of treatment (alum coagulation and softening) on HAA formation is also necessary. A better understanding of the influence of each of these variables will allow utilities that chloraminate to make more informed corrective treatment changes to minimize distribution system DXAA concentrations.

4.2. WATER CHARACTERISTICS

The characteristics of the source and treated waters are summarized in Table 4-1. Lake Austin and Metedeconk River source waters had moderate DOC concentrations (3.74 mg/L and 4.32 mg/L, respectively) and Biscayne Aquifer and St. Paul source waters had very high DOC concentrations (11.95 mg/L and 11.01 mg/L). Lake Austin and St. Paul source water had a relatively low SUVA of about 2.5, which can be used to characterize the reactivity of the NOM with respect to DBP formation, while the other source waters had higher SUVAs of approximately 3.5. The NOM characterizations shown in Table 4-1 suggest that the organic carbon in Biscayne Aquifer water was

predominantly hydrophobic. A relatively large fraction of the organic carbon in St. Paul source water was hydrophobic as well, while the Lake Austin and Metedeconk River source water contained a moderate amount of hydrophobic DOC.

Table 4-1 - Water quality characteristics for the various source and treated waters tested

Parameter	LA Source	LA Soft.	MR Source	MR Coag.	BA Source	BA Soft.	SP Source	SP Soft.
pH	8.2	9.7	6.78	7.25	7.53	9.61	8.0	9.6
DOC (mg/L)	3.74	3.32	4.32	2.31	11.95	9.45	11.01	6.60
Hydrophobic DOC (%)	50	49	51	51	78	74	59	69
Transphilic DOC (%)	17	16	15	24	23	27	ND	ND
Hydrophilic DOC (%)	20	20	15	20	10	11	41	40
AMW < 3K (mg DOC /L)	1.31	126	1.42	1.7	5.1	2.97	6.74	3.09
AMW > 3K (mg DOC /L)	2.67	2.06	1.78	.47	6.85	6.48	4.33	3.51
UFC/SUFC HAA_9 (µg/L)	90.2*	58.1†	219*	65.0*	234*	170†	ND	ND
Bromide (µg/L)	168	164	33	49	100	135	6.9	12
SUVA (L/mg-m)	2.49	2.05	3.87	1.68	3.45	2.90	2.45	1.55
Ambient Br^- /DOC (µg/mg)	44.9	49.4	7.6	21.2	8.4	14.3	0.6	1.8

* = UFC, † = SUFC

ND = Not determined

LA = Lake Austin, Austin, TX; MR = Metedeconk River, Brick Township, NJ; BA = Biscayne Aquifer, Boca Raton, FL; SP = St. Paul, MN; Coag. = coagulated; Soft. = softened

The reactivity of the source waters was measured by chlorination under uniform formation conditions. Chlorination of Biscayne Aquifer and Metedeconk River source waters under these conditions produced similar concentrations of HAA_9 while Lake Austin source water formed considerably less. The organic carbon concentrations, however, vary dramatically between water sources; therefore, reactivity is better characterized on a yield basis. The Metedeconk River source water, which yielded 50.7 µg HAA_9/mg DOC, was the most reactive of the source waters studied, while the Lake Austin source was considerably less reactive (24.1 µg HAA_9/mg DOC). Biscayne Aquifer source water, which formed the greatest concentration of HAA_9 under the UFC test, was the least reactive, producing less than 20 µg HAA_9/mg DOC.

The source waters selected also span the typical range of bromide concentrations (Amy *et al.,* 1993): St. Paul and Metedeconk River had low bromide concentrations of 6 µg/L and 33 µg/L, repectively, while Biscayne Aquifer had a moderate bromide concentration of 100 µg/L, and Lake Austin had a high bromide concentration of 168 µg/L.

Treatment had a significant impact on the water characteristics. Alum coagulation of Metedeconk River water removed approximately 47% of the DOC concentration, whereas softening was less effective for Lake Austin water, removing only 11%. In addition, softening only caused an 18% SUVA reduction in Lake Austin, whereas alum coagulation of Metedeconk River resulted in SUVA decrease of 56%. Higher SUVA values indicate greater humic content and increased susceptibility to coagulation (Edzwald 1993). Edzwald (1993) also noted that waters with relatively high SUVA values should achieve DOC removals of 50% or greater during coagulation. Therefore, the DOC removal achieved from coagulation of Metedeconk River water was expected. The reactivity of the treated waters was also measured using the UFC or the

SUFC test where appropriate. Treatment reduced the HAA_9 formation resulting from chlorination in all of the treated waters studied. Alum coagulation of Metedeconk River dramatically decreased HAA_9 formation, forming only 30% of that in the source water. Softening Lake Austin water had a lesser impact on HAA_9 formation. The treated water formed 64% of the source water HAA_9 formation.

4.3. RELATIVE IMPORTANCE OF FACTORS IN DXAA FORMATION

The key objective of the fractional factorial batch experiments was the identification of the water quality and chloramination variables that are most important in DXAA formation. In these experiments, outlined in Section 3.2, Metedeconk River and Lake Austin waters were studied. The ANOVA calculations were performed on a molar basis to weight all three DXAAs equally (bromine-substituted species weigh more than their chlorine-substituted counterparts).

A summary of the relative significance and contribution of each evaluated factor studied in the initial batch screening experiments in Lake Austin water is provided in Figure 4-1. The waters screened included source, softened, and source water collected during a period of algal bloom, as well as the hydrophilic fraction of the source water.

In all the Lake Austin waters studied, pH and bromide concentration were the two most significant contributors to DXAA formation over the range of conditions studied. After pH and bromide, Cl_2/N mass ratio was the next most significant contributor to DXAA formation, accounting for approximately 12 percent of the formation. Temperature and chloramine residual also impacted DXAA formation, but were much less influential than the aforementioned factors, generally accounting for 5 percent or less of the DXAA formation.

The percent contribution of the error, or unexplained variation of the ANOVA analysis, was typically less than 15%, meaning that no significant variables contributing

to DXAA formation were omitted, and therefore, the experiment was performed and analyzed under reasonably controlled conditions (Ross 1988). Since three of the four Lake Austin waters tested maintained errors less than 15%, the higher unexplained variation in the source water (25%) may indicate that the source water had a wider variety of NOM for example, than the other waters studied, or may also be a result of greater experimental error.

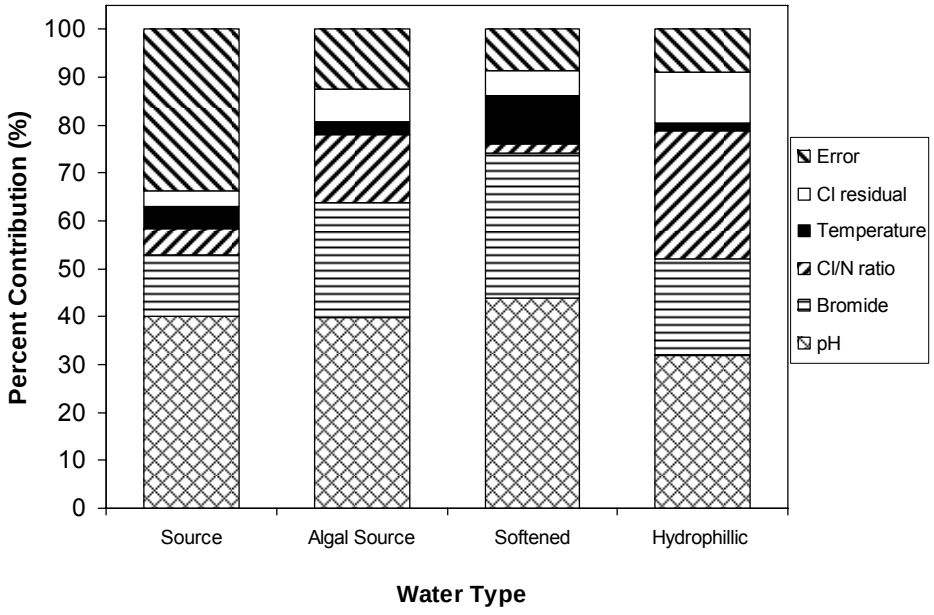


Figure 4-1 – ANOVA results for Lake Austin waters (μmol/L)

A summary of the Metedeconk River water batch screening experiments is provided in Figure 4-2, which represent the ANOVA results for all the waters screened, including source, alum coagulated, biodegraded, < 3K AMU, and the hydrophilic fraction of the source water.

In general, the two most significant factors in DXAA formation over the range of conditions studied were again pH and bromide concentration, although temperature was an important factor in the water that underwent biodegradation. Analogous to Lake

Austin water, Cl_2/N mass ratio typically was the most significant contributor to DXAA formation after pH and bromide, on average accounting for about 10 or 13 percent of the variation in DXAA formation. However, in two of the seven waters (coagulated and < 3K AMU) the contribution of Cl_2/N ratio was greater than that of the bromide concentration. Unlike Lake Austin water, however, temperature played a larger role in DXAA formation, contributing on average 7 or 10 percent for mass or molar ANOVA based calculations, respectively, and accounting for greater than 18% of the formation in the biodegraded water. Again, as with Lake Austin water, the contribution from the chloramine residual was minimal, generally accounting for 6 percent or less of the DXAA formation. The unexplained variation of the ANOVA analyses was again controlled satisfactorily, with only two of the experimental data sets having errors greater than 20%.

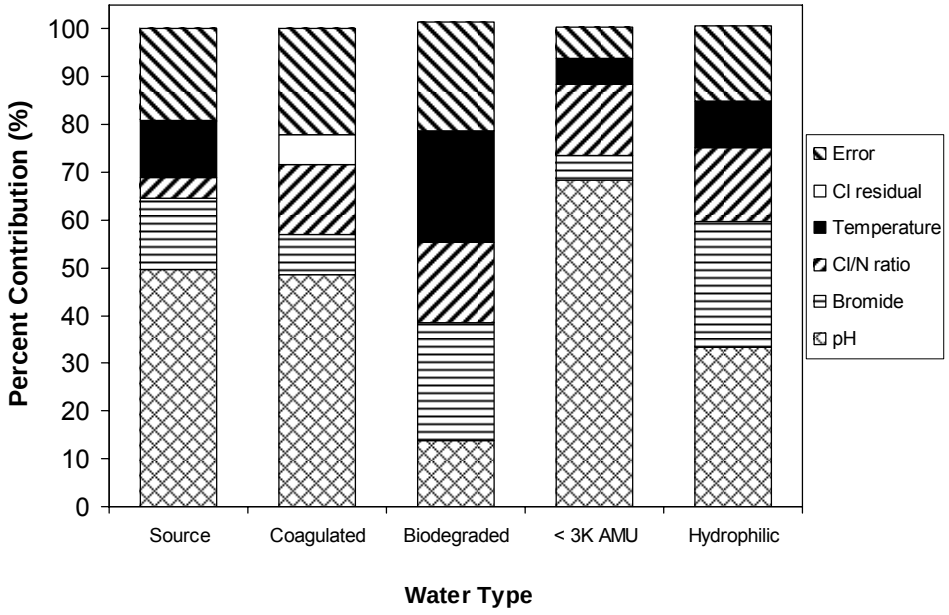
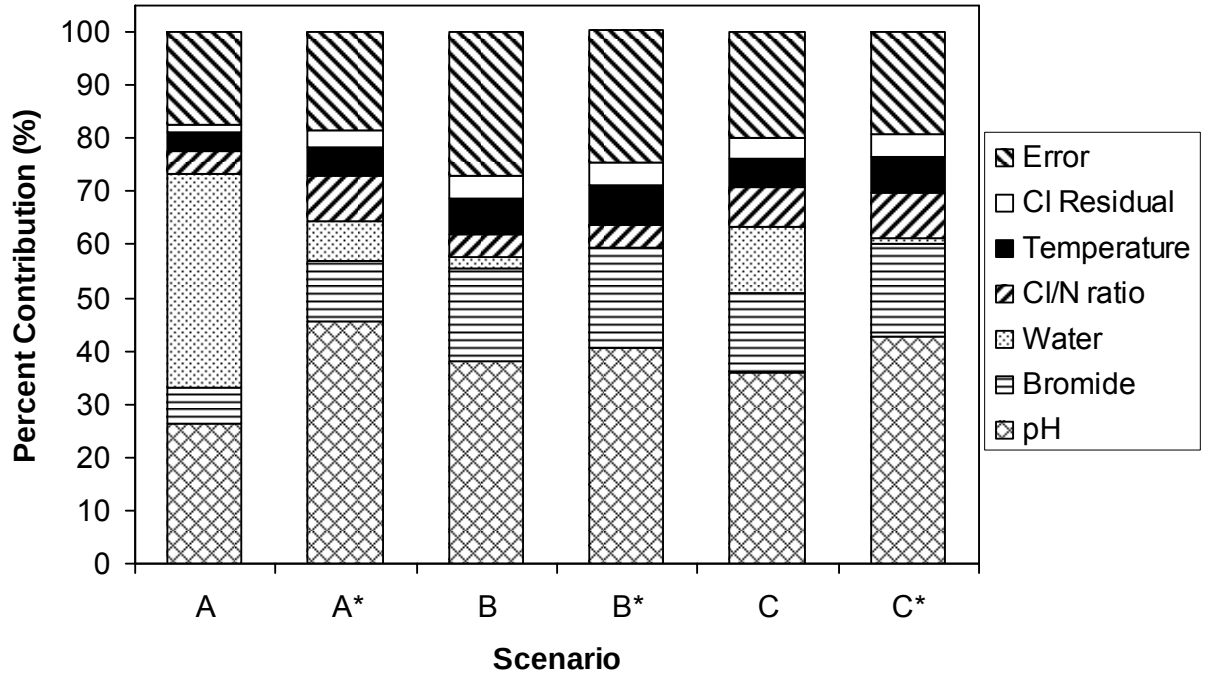


Figure 4-2 – ANOVA results for Metedeconk River waters (µmol/L)

The differences in source waters, treatments, and NOM fractions also have a significant influence on DXAA formation. ANOVA analyses of several scenarios combining the trials of the individual experiments were considered to characterize the impact of treatment as well as differences in source waters (Figure 4-3). Alum coagulation of Metedeconk River water (Scenario A) had a significant impact on DXAA formation based upon the large contribution from the "water" factor of the ANOVA analysis. Softening Lake Austin water (Scenario B) had minimal influence. This difference may be related to TOC removal; minimal TOC removal (15%) was achieved from softening Lake Austin water, whereas coagulation of Metedeconk River water resulted in a much greater TOC removal (36%).



A: Metedeconk River, NJ source and alum coagulated
B: Lake Austin, TX source and softened
C: Metedeconk River, NJ source; Lake Austin, TX source and algal source

* indicates ANOVA performed on a molar yield basis

Figure 4-3 ANOVA results for various combinations of waters on both a molar concentration (μmol DXAA/L) and molar yield basis (μmol DXAA/mg DOC)

Another aspect of HAA formation is the significance of source water precursor content (*e.g.*, NOM and SUVA), both spatially and temporally. Scenario C shows the influence of source water quality characteristics, comparing Metedeconk river source water with both Lake Austin source waters. This scenario indicates that source water variability had a significant impact on DXAA formation, based on the contribution from the "water" factor.

HAA formation is strongly influenced by DOC concentration, which varied from experiment to experiment depending upon the water treatment or fraction tested. To determine if observed differences in DXAA formation were truly related to differing reactivity of the waters or just a reflection of DOC concentrations, DXAA yields were studied. Examination of DXAA yields (μmol DXAA/mg DOC) in essence is a normalization approach to account for the different DOC concentrations. In Figure 4-3, Scenarios A*, B*, and C* indicate the ANOVA analyses performed on a molar yield basis. This comparison made the effect of treatment and the different contributions of the various NOM fractions to DXAA formation much less influential. The ANOVA results, analyzed on a molar yield basis, revealed that softening Lake Austin water did not have a significant effect on DXAA yield (Scenario B*), and similarly, when analyzed on a molar basis, the "water" factor contributed approximately 2% (Scenario B) to the variation in the DXAA data. Coagulating Metedeconk River water, however, had a more significant impact. The ANOVA results on a molar yield basis indicate that water quality in coagulated Metedeconk River water contributed approximately 8% (Scenario A*), whereas it accounted for about 40% on a molar basis (Scenario A). Although the contribution on a molar yield basis was considerably smaller, the 8% contribution to the DXAA formation was still significant (greater than 99% confidence), and as such, demonstrates that treatment of Metedeconk River water decreased the reactivity of remaining NOM. In contrast, the insignificance of the "water" factor in the Lake Austin ANOVAs shows that treatment had no appreciable effect on NOM reactivity.

Consideration of the three source waters on a molar yield basis (Scenario C*) showed an insignificant contribution (approximately 1%) from the "water" factor of the ANOVA. When analyzed on a molar basis (Scenario C), however, the "water" factor contributed 13% and was statistically significant. Again, the difference in significance of

the "water" factor between the two examples can be attributed to normalizing the DOC concentration. This normalization approach indicated that the reactivity of the source waters during chloramination was similar, which is in contrast to the large difference in reactivity between the Lake Austin and Metedeconk River source waters during chlorination (Table 4-1).

4.4. ROLE OF pH AND BROMIDE CONCENTRATION IN DXAA FORMATION

The ANOVA analysis of the initial batch screening experiments indicated that pH and bromide were the two most significant variables contributing to DXAA formation over the range of conditions studied for the waters tested. To better characterize the contribution of pH and bromide on DXAA formation, the data were analyzed on a molar yield basis. In each initial batch screening experiment, two different pH values (pH 7 and 9) and two different bromide concentrations (ambient and ambient + 0.5 mg/L) were used. Therefore, the 16 trials of each experiment fell into four groups of four trials, each based on the four combinations of these factors in each experiment. DXAA yield was examined across all 16 trials and within the four groups to discern the impact of the major factors on DXAA yield.

The molar DXAA yields for the experiments with Lake Austin and Metedeconk River water are shown in Figure 4-4. The data in all four experiments show the largest DXAA yield with bromide addition at pH 7 and the smallest DXAA yield with the ambient bromide concentration at pH 9. Softening Lake Austin water only changed the yields to a small extent, indicating that softening did not preferentially remove DXAA precursors. However, alum coagulating Metedeconk River water was beneficial in decreasing the yields, indicating preferential removal of DXAA precursors.

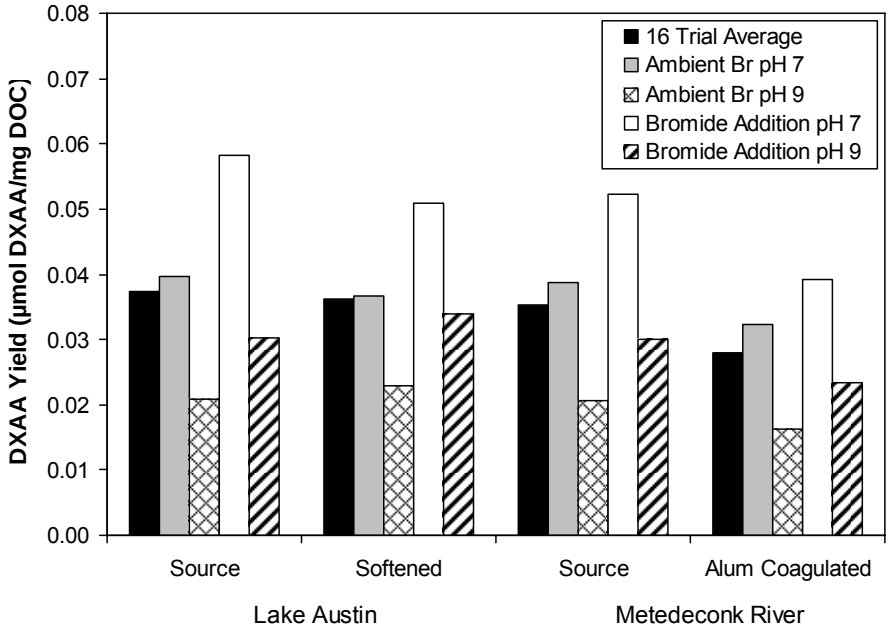


Figure 4-4 Molar DXAA yield in Lake Austin and Metedeconk River water

The fractional factorial batch experiments revealed that pH, bromide concentration, and water source were influential factors in DXAA formation. DOC and SUVA are often used as surrogate parameters for characterizing or estimating the reactivity of a water source. Thus, to complement the waters studied in the fractional factorial batch experiments, additional water sources were selected to further diversify the range of source water DOC studied. To investigate the potential non-linear effects of the most influential variables, three different levels of pH (7, 8, and 9) and three different Br^-/DOC ratios (<15, 40, and 87.5 µg/mg) were studied. The influence of these two variables is illustrated in Figure 4-5. In general, the DXAA molar yield decreased as the pH increased for all of the Br^-/DOC ratios studied. Regardless of the pH, the Br^-/DOC ratio had a minimal influence on DXAA molar yield of the waters tested. These results were somewhat unexpected as the ANOVA from the initial batch screening experiments

revealed that bromide had a significant influence on DXAA formation. However, the range of Br^-/DOC ratios used in the initial batch screening experiments was greater than in the follow-up batch screening experiments, where the Br^-/DOC levels were lower and more representative of the range of typical drinking water sources. Thus, very high bromide or Br^-/DOC ratios will affect DXAA yield, but small effects should be observed over the range of typical practice.

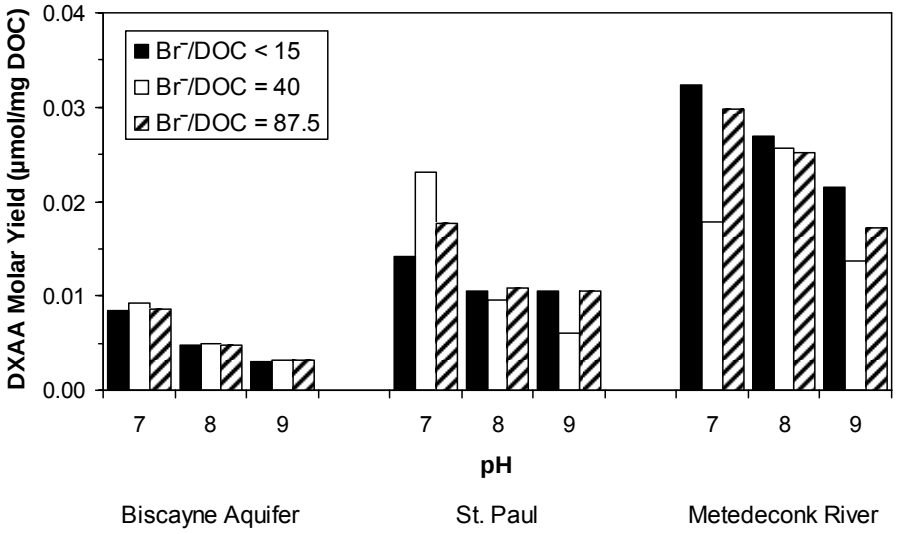


Figure 4-5 Effect of pH and Br^-/DOC ratio on Biscayne Aquifer, St. Paul, and Metedeconk River source waters.

4.5. INFLUENCE OF NOM CHARACTERISTICS

Various NOM characteristics, water quality parameters, and chloramination conditions were monitored during this study, which permitted the assessment of DXAA formation as a function of a diversity of variables. In most of the literature, XAD-8 non-ionic resins are used to separate the hydrophobic and hydrophilic fractions. Because the transphilic fraction is included in the hydrophilic fraction, a further separation step is sometimes undertaken to isolate the transphilic fraction from the hydrophilic fraction.

Fractionation is discussed here based on XAD-8 separation only; therefore, the transphilic fraction is included in the hydrophilic fraction.

Many water quality characteristics such as DOC, UV, SUVA, SUVA x Br^-, hydrophilic DOC, and hydrophobic DOC were considered and plotted against DXAA formation to search for meaningful relationships. However, none of the aforementioned water quality characteristics yielded significant correlations with DXAA formation. Previous research (Symons *et al*., 1998; Singer *et al*., 1999) suggested that a relationship between DXAA yield and SUVA might exist, but this research did not support the significance of such a relationship. However, a correlation between the DXAA mass yield and the hydrophilic fraction was observed (Figure 4-6). In general, DXAA mass yield increased as the hydrophilic DOC/Total DOC ratio increased, suggesting that the hydrophilic fraction preferentially contributed to DXAA formation. Given the substantial reactivity of the hydrophilic fraction, as demonstrated recently by others (Hwang *et al*., 2000) and these experiments, the absence of a relationship between DXAA yield and SUVA is to be expected when comparing waters from different sources. Nevertheless, a strong correlation exists between SUVA and the aromatic carbon content of NOM (Croue *et al.,* 1999). Therefore, SUVA can be used to estimate the relative proportion of hydrophobic acids (i.e., humic substances) in a water, because humic substances are known to be the most aromatic NOM fraction (Martin-Moussett *et al.,* 1997; Leenheer and Croue 2003). SUVA remains an important parameter because higher SUVA values indicate an increased susceptibility to coagulation (Edzwald 1993). Edzwald (1993) also noted that waters with relatively high SUVA values should achieve DOC removals of 50% or greater during coagulation, which should lead to less DXAA formation.

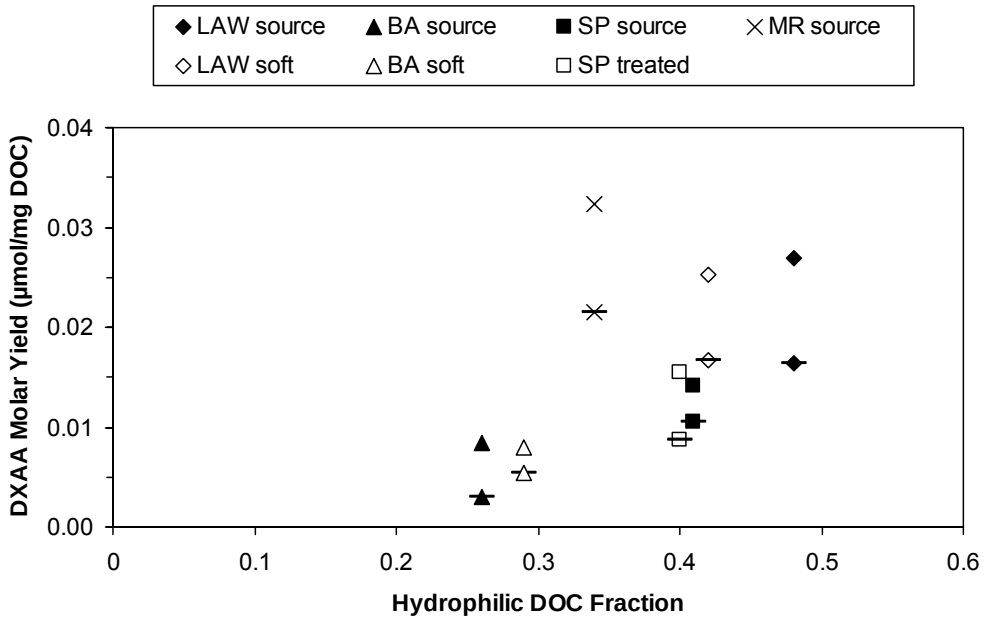


Figure 4-6 Effect of hydrophilic/DOC ratio and pH on DXAA molar yield (line through data point indicates pH 9; no line through data point indicates pH 7)

4.6. OTHER FACTORS

The effect of temperature on DXAA formation at different pH and Cl_2/N ratios was investigated with Lake Austin softened water (Figure 4-7). Temperature had little effect at the 3/1 Cl_2/N mass ratio. In addition, at 70 °F the Cl_2/N ratio had little effect on DXAA formation. At 85 °F, however, DXAA formation increased as the Cl_2/N ratio increased; the increased DXAA formation was especially apparent at the 5/1 Cl_2/N mass ratio. Therefore, the influence of temperature on DXAA formation is likely dependent on other chloramination conditions such as pH and Cl_2/N ratio.

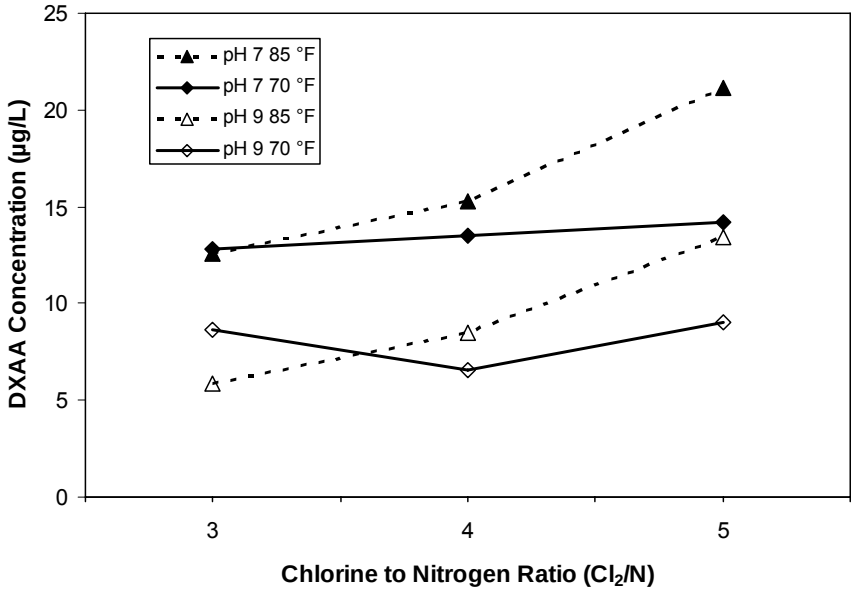


Figure 4-7 Effect of temperature and Cl_2/N ratio on DXAA formation in softened Lake Austin water (2 mg/L residual; 48 hour incubation)

Symons *et al*. (1998) studied the impact of chloramine residual concentration on DBP formation in three source waters. Over a broad range of pH and Cl_2/N ratios no relationship between residual concentration (1, 2, and 4 mg/L) and DBP formation was apparent in 48-hour simulated distribution system (SDS) tests. More rigorous statistical analyses of this extensive data set also failed to show any statistically significant relationship between DBP formation and chloramine residual concentration (Diehl, 2000). Thus, the available data suggest that residual concentration is of secondary importance in DBP formation over the range of concentrations typical in practice. The ANOVA analysis of the batch screening experiments indicated that the chloramine residual was of minimal significance to DXAA formation in comparison to pH and bromide concentration, and therefore supports the above conclusion. In addition to the ANOVA, DXAA concentrations were averaged across all 16 trials of each batch

screening experiment to show the impact of a selected factor, even as other factors may vary. Figure 4-8 indicates that increasing the chloramine residual concentration from 2 to 4 mg/L resulted in average percent increases in DXAA formation ranging from 10-25%. Although the ANOVA analysis showed chloramine residual to be a relatively insignificant contributor, an impact was, nevertheless, still observable.

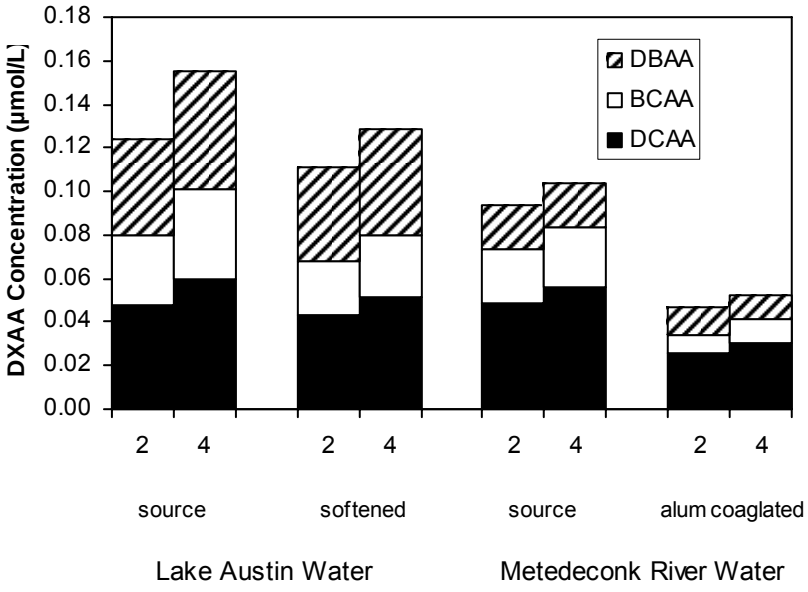


Figure 4-8 Effect of chloramine residual on DXAA formation

4.7. BROMINE INCORPORATION

DXAA speciation also is of interest as the health effects of bromine-substituted HAAs may be of more concern (Bull *et al.,* 1995; Karagalioglu *et al.,* 2000; Karagalioglu *et al.,* 2002). Previous research (Diehl *et al.,* 2000) introduced the factor, n', to describe the degree of bromine substitution of HAAs, which is analogous to the factor, n, used to characterize the degree of bromine substitution of trihalomethanes. These parameters are the average number of bromine molecules in the total HAAs and THMs, respectively, and can range from zero to three. In this research, the factor, n_D', was used to

characterize the bromine substitution of DXAAs. The value of n_D' can range from zero (all DCAA) to two (all DBAA). Figure 4-9 shows the influence of bromide and pH on n_D'in Lake Austin and Metedeconk River source and treated waters. As expected, n_D' was greater in the trials with bromide addition. In addition, a greater degree of bromine incorporation was observed at pH 7 than at pH 9. The fractional factorial experiments also permitted an assessment of the relative influence of each parameter in bromine incorporation. ANOVA analysis indicated that both bromine concentration and pH were significant in contributing to the observed variations in n_D'. In general, bromide concentration accounted for approximately 70% of the observed variation, and pH accounted for about 15%, while the unexplained variation, or error, was limited to less than 15%.

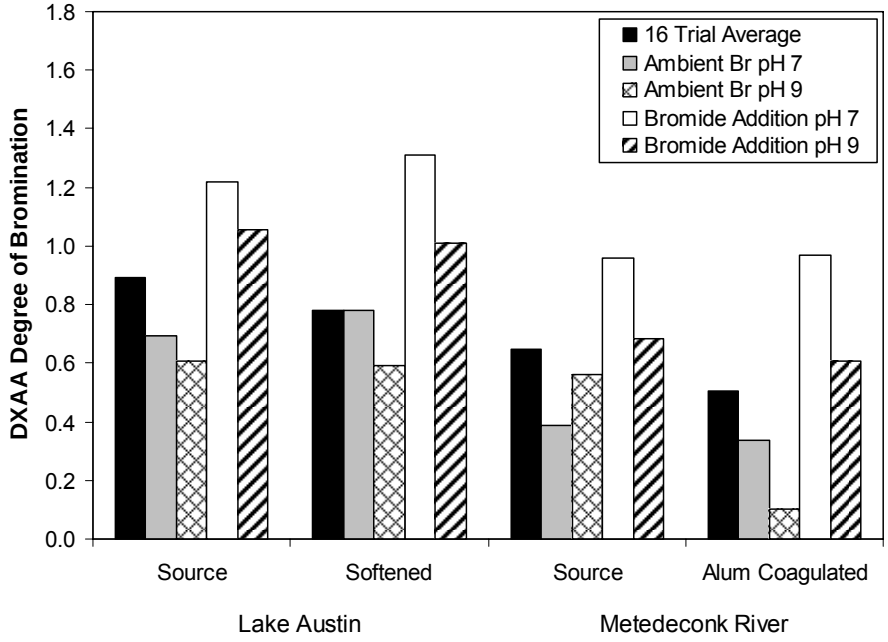


Figure 4-9 Bromine incorporation in Lake Austin and Metedeconk River waters

The presence of bromide substantially increases the range of possible halogenated species that react with NOM and can be incorporated into DBPs. The bromine-substituted haloamines, which potentially include monobromamine, dibromamine, and bromochloramine, and free bromine may be in competition with their chlorine-substituted counterparts for available NOM reactive sites. To further evaluate the bromine substitution of DXAAs, the effect of both bromine to average chloramine molar ratios (Br^-/average Cl^+) and Br^-/DOC ratios were investigated with the batch screening experimental data. Symons *et al*. (1993) investigated the influence of these two ratios on bromine substitution during chlorination; higher Br^-/DOC and Br^-/average Cl^+ ratios led to greater bromine incorporation into DBPs. Figure 4-10 illustrates the influence of Br^-/average Cl^+ molar ratios, as well as pH, on the degree of bromine incorporation into DXAAs. Increases in Br^-/average Cl^+ caused an increase in DXAA bromine incorporation in each of the waters evaluated. The Br^-/DOC ratio had a similar effect on bromine incorporation (Figure 4-11), and as before, higher relative concentrations of bromine-substituted species formed at lower pH. The influence of either Br^-/average Cl^+ or Br^-/DOC ratio on n_D' varies significantly among the different sources, indicating that differences in NOM may play a crucial role in bromine-substitution.

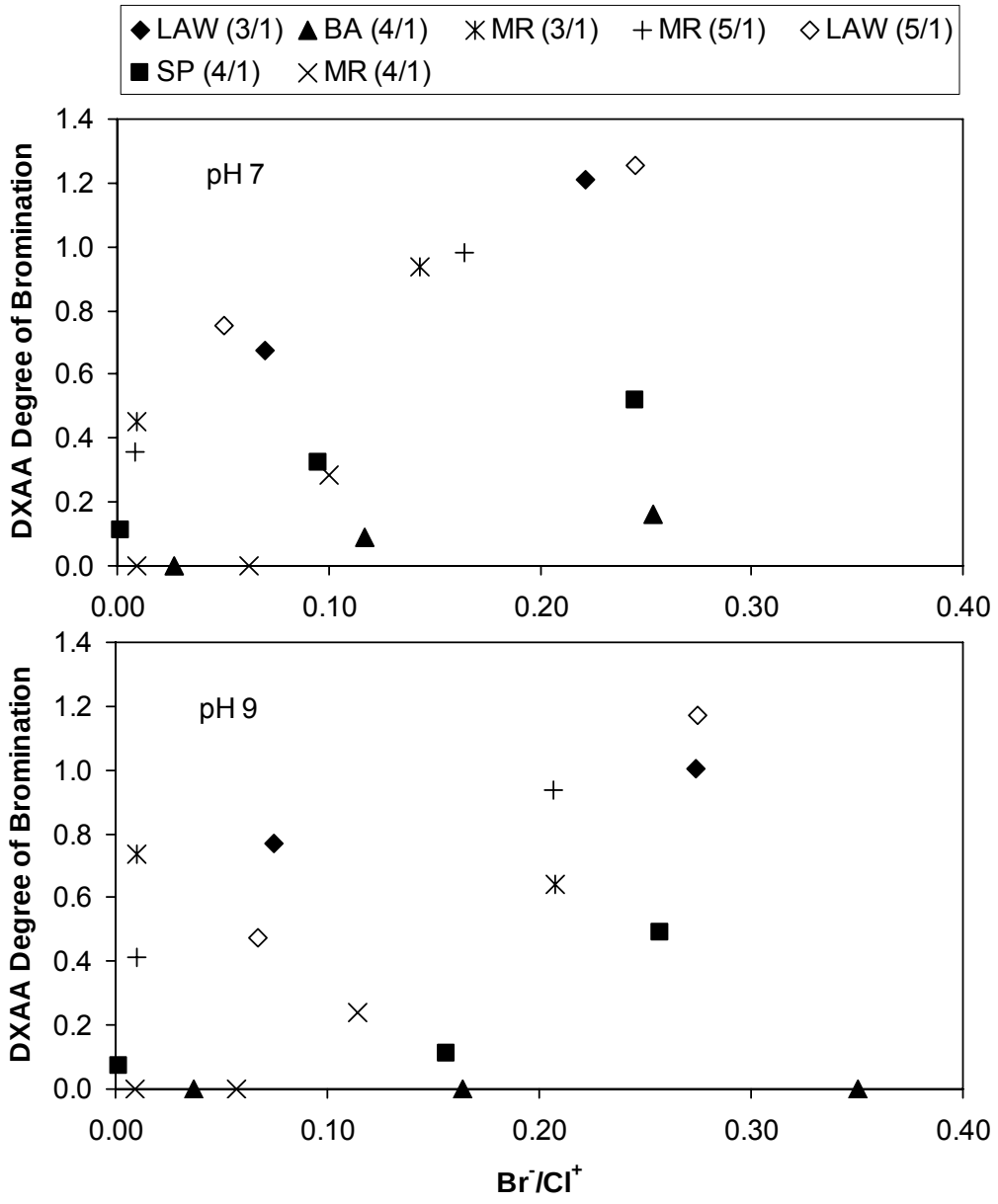


Figure 4-10 Effect of bromine to average chloramine concentration ratio (µmol Br^-/µmol Cl_2) on DXAA degree of bromine-substitution in various source waters (2 mg/L chloramine residual; 48-hour incubation; parenthesis indicate Cl_2/N mass ratio)

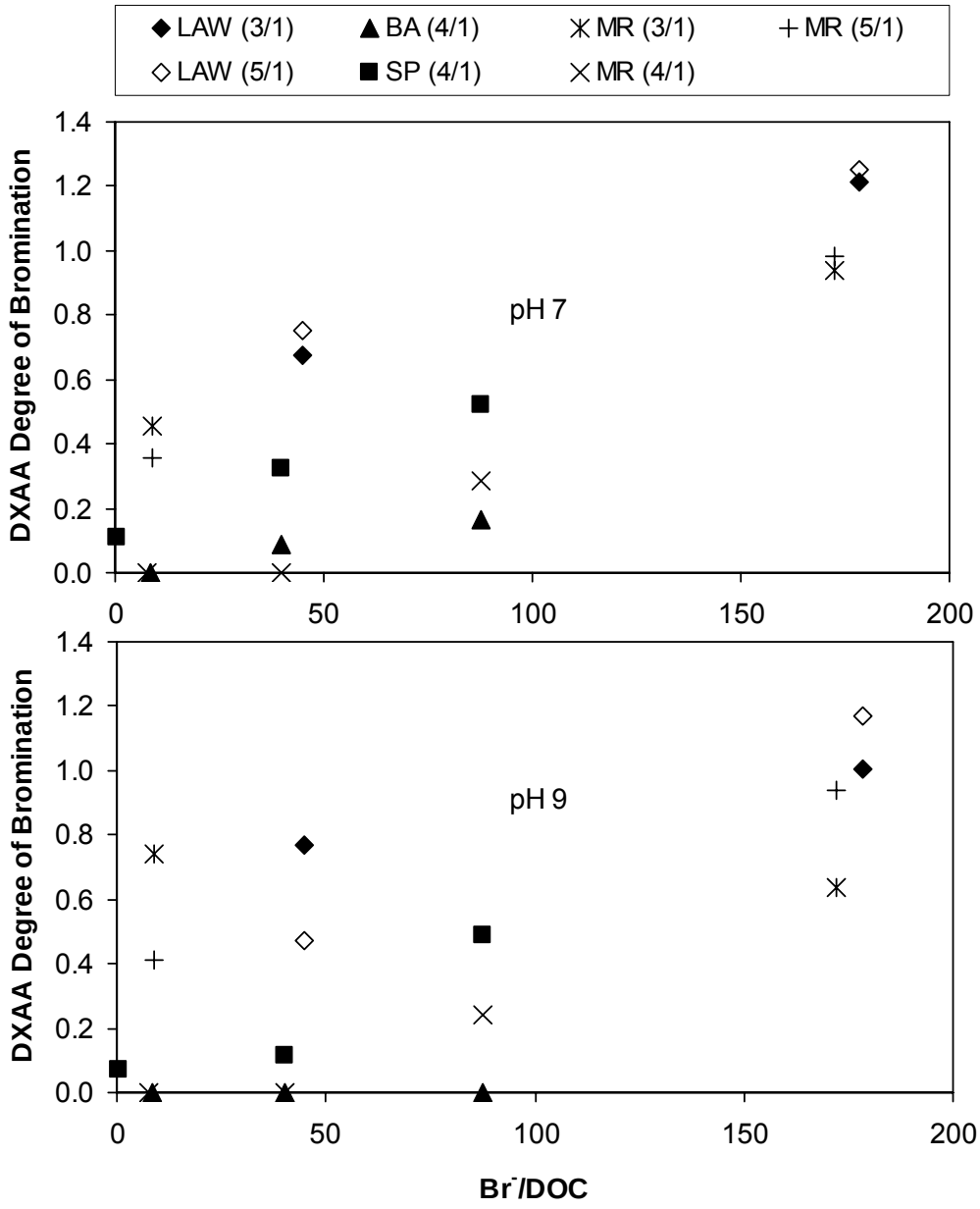


Figure 4-11 Effect of bromine to DOC ratio (µg Br^-/mg DOC) on DXAA degree of bromine-substitution in various source waters (2 mg/L chloramine residual; 48-hour incubation; parenthesis indicate Cl_2/N mass ratio)

4.8. SUMMARY

The influence of NOM characteristics, pH, bromide concentration, Cl_2/N ratio, temperature, and chloramine residual on DXAA formation was studied in four diverse water sources. ANOVA analyses of DXAA formation in Lake Austin and Metedeconk River over a broad variety of experimental conditions usually pointed to pH as being the most significant factor in DXAA formation. DXAA formation decreased as the pH increased. Therefore, utilities interested in decreasing DXAA formation should first examine the possibility of raising the pH of their water.

The impact of bromide can be viewed from several perspectives: the DXAA mass concentration or yield, DXAA molar concentration or yield, and DXAA speciation, which can be described by n_D'. Generally, bromide impacts the DXAA speciation and DXAA mass concentration or yield more so than DXAA molar concentration or yield. A shift in speciation to the bromine-substituted species occurred as the bromide concentration increased and the pH decreased. Because of the higher molecular weight of bromine in comparison to chlorine, the shift in speciation implies an increase in the DXAA mass yield or concentration. The overall results suggest that the DXAA molar yield generally will not increase over the range of Br^-/DOC ratios typical of practice. A source water experiencing a large increase in bromide concentration, however, may exhibit an increase in the DXAA molar yield. An increase in the Br^-/DOC ratio is undesirable from two perspectives. First, the regulations are based on mass concentration, so the likelihood of violating the HAA MCL increases. Second, the bromine-substituted HAAs may be of greater health concern.

ANOVA analyses indicated that the Cl_2/N mass ratio was the next most significant contributor to DXAA formation after pH and bromide. DXAA formation decreased as the Cl_2/N ratio decreased. Temperature and chloramine residual also

impacted DXAA formation, but were much less influential than the aforementioned factors. DXAA formation increased as the temperature increased, and the impact of temperature was more pronounced as the Cl_2/N ratio increased.

NOM characteristics and concentration, and treatment processes that remove NOM, can also have a significant effect on DXAA formation. NOM in the hydrophilic fraction was more reactive in forming DXAA than the NOM in the hydrophobic fraction. The effectiveness of treatment on DXAA formation is largely related to overall DOC removal, although preferential removal of more reactive NOM fractions also may contribute to reduced DXAA formation. Thus, in addition to pH adjustment, reducing the organic precursor concentrations as much as possible is another strategy that may be effective in controlling DXAA formation. On the other hand, treatment processes that remove DOC will increase the Br^-/DOC ratio, which will shift the DXAA speciation more toward the bromine-substituted species and in some cases may increase the DXAA yield.

CHAPTER 5: DXAA Formation Kinetics

5.1. INTRODUCTION

The rate of DXAA formation during chloramination is a key consideration in determining strategies for minimizing formation. In addition, the impact of short periods of prechlorination on subsequent DXAA formation kinetics during chloramination is largely unexplored, but likely to be of major consequence. Batch kinetic experiments were conducted to discern the impacts of certain water quality and chloramination variables, as well as the impact of prechlorination, on DXAA formation. A better understanding of DXAA formation kinetics with chloramines is needed as an important input to the complicated decision-making process facing some utilities.

5.2. WATER CHARACTERISTICS.

Both source and treated water from four different locations were studied to discern the impact of pH, bromide concentration, temperature, and treatment on DXAA formation kinetics. The characteristics of each of these waters are summarized in Table 5-1. DOC is often used as a measurement of NOM: Lake Austin and Metedeconk River source waters have moderate DOC concentrations (3.74 mg/L and 4.32 mg/L, respectively), Charleston source water has a higher DOC concentration (5.11 mg/L), and Biscayne Aquifer source water has a very high DOC concentration (11.95 mg/L). The NOM characterizations shown in Table 5-1 suggest that the organic carbon in Biscayne Aquifer water was predominantly hydrophobic. A relatively large fraction of the organic carbon in Charleston source water was hydrophobic as well, while the Lake Austin and Metedeconk River source water contained a moderate amount of hydrophobic DOC. Lake Austin source water had a relatively low SUVA of 2.49, which can be used to

characterize the reactivity of the NOM with respect to DBP formation, while the other source waters had higher SUVAs of approximately 3.5.

Table 5-1 – Water quality characteristics

Parameter	LA Source	LA Soft	MR Source	MR Coag	BA Source	BA Soft	Chl Source	Chl Coag
pH	8.2	9.7	6.78	7.25	7.53	9.61	7.2	6.5
DOC (mg/L)	3.74	3.32	4.32	2.31	11.95	9.45	5.11	2.55
Hydrophobic DOC (%)	50	49	51	51	78	74	66	54
Transphilic DOC (%)	17	16	15	24	23	27	ND	ND
Hydrophilic DOC (%)	20	20	15	20	10	11	ND	ND
UFC/SUFC HAA_9 (µg/L)	90.2*	58.1†	219*	65.0*	234*	170†	216*	72.5*
Bromide (µg/L)	168	164	33	49	100	135	183	174
SUVA (L/mg-m)	2.49	2.05	3.87	1.68	3.45	2.90	3.48	1.59
Ambient Br^-/DOC (µg/mg)	44.9	49.4	7.6	21.2	8.4	14.3	35.8	68.2

* = UFC, † = SUFC

ND = Not determined

LA = Lake Austin, Austin, TX; MR = Metedeconk River, Brick Township, NJ; BA = Biscayne Aquifer, Boca Raton, FL; Chl = Charleston, SC, Soft = softened, Coag = coagulated

The reactivity of the source waters was also measured by chlorination under uniform formation conditions. Chlorination of Biscayne Aquifer, Metedeconk River, and Charleston source waters under these conditions produced similar concentrations of HAA_9 while Lake Austin source water formed considerably less. The organic carbon concentrations, however, vary dramatically between water sources; therefore, reactivity is

better characterized on a yield basis. The Metedeconk River source water, which yielded 50.7 µg HAA_9/mg DOC, was the most reactive of the source waters studied. The Charleston source water was also rather reactive, yielding 42.3 µg HAA_9/mg DOC, while the Lake Austin source was considerably less reactive (24.1 µg HAA_9/mg DOC). Biscayne Aquifer source water, which formed the greatest concentration of HAA_9 under the UFC test, was the least reactive, producing less than 20 µg HAA_9/mg DOC.

The source waters selected also span the typical range of bromide concentrations (Amy *et al.,* 1993): Metedeconk River had a low bromide concentration of 33 µg/L, while Biscayne Aquifer had a moderate bromide concentration of 100 µg/L, and Lake Austin and Charleston source waters had high bromide concentrations of 168 µg/L and 183 µg/L, respectively. The Br^-/DOC ratio can be used to estimate the amount of bromine that will be incorporated into the HAAs. Lake Austin and Charleston source waters had much higher Br^-/DOC ratios (44.9 µg/mg and 35.8 µg/mg, respectively) than Metedeconk River and Biscayne Aquifer source waters (7.6 µg/mg and 8.4 µg/mg, respectively); therefore, Lake Austin and Charleston waters should have a greater tendency to form bromine-substituted HAAs.

Treatment had a significant impact on the water characteristics. Alum coagulation of Charleston and Metedeconk River water removed approximately 50% and 47% of the DOC concentration, respectively, whereas softening was less effective for Biscayne Aquifer and Lake Austin water, removing only 21% and 11%, respectively. In addition, softening only caused a 16% SUVA reduction in Biscayne Aquifer and an 18% SUVA reduction in Lake Austin, whereas alum coagulation on Metedeconk River and Charleston waters resulted in SUVA decreases of 56% and 54%, respectively. Higher SUVA values indicate greater humic content and increased susceptibility to coagulation (Edzwald 1993). Edzwald (1993) also noted that waters with relatively high SUVA

values should achieve DOC removals of 50% or greater during coagulation. Therefore, the DOC removal achieved from coagulation of Metedeconk River and Charleston source waters was expected. The reactivity of the treated waters was also measured using the UFC or the SUFC test where appropriate. Treatment reduced the HAA_9 formation in all of the treated waters studied. Alum coagulation of Metedeconk River and Charleston dramatically decreased HAA_9 formation, forming only 30% and 34% of that in the source waters, respectively. Softening of Lake Austin and Biscayne Aquifer waters had a lesser impact on HAA_9 formation. The treated waters formed 64% and 73% of the source water HAA_9 formation, respectively.

5.3. CHLORAMINATION

Water from four different sources was used to determine the impact of pH, bromide concentration, temperature, and treatment on DXAA formation kinetics during traditional chloramination (simultaneous ammonia and chlorine addition). In these experiments, described in Chapter 3, waters were dosed to achieve a 4/1 Cl_2/N mass ratio and a target chloramine residual of 2 mg/L at 48 hours, which is typical of drinking water treatment plants in practice.

Kinetics and speciation of the DXAA formation in Metedeconk River source water are illustrated in Figure 5-1. The DXAA formation was characterized by an initial rapid period of formation followed by a period of slower formation. Approximately 32% of the 72-hour DXAA concentration formed after only 5 minutes and 40% formed after 1 hour. Similar DXAA formation kinetics were observed in the other waters studied. Metedeconk River source water has a low bromide concentration (33 µg/L), and thus a low Br^-/DOC ratio (8 µg/mg). Therefore, DCAA was the predominant dihalogenated species that formed; minimal formation of bromine-substituted DXAAs (bromochloroacetic acid, BCAA and dibromoacetic acid, DBAA) was observed. Source

waters with higher ambient bromide concentrations, such as Lake Austin and Charleston, exhibited greater bromine-substituted DXAA formation.

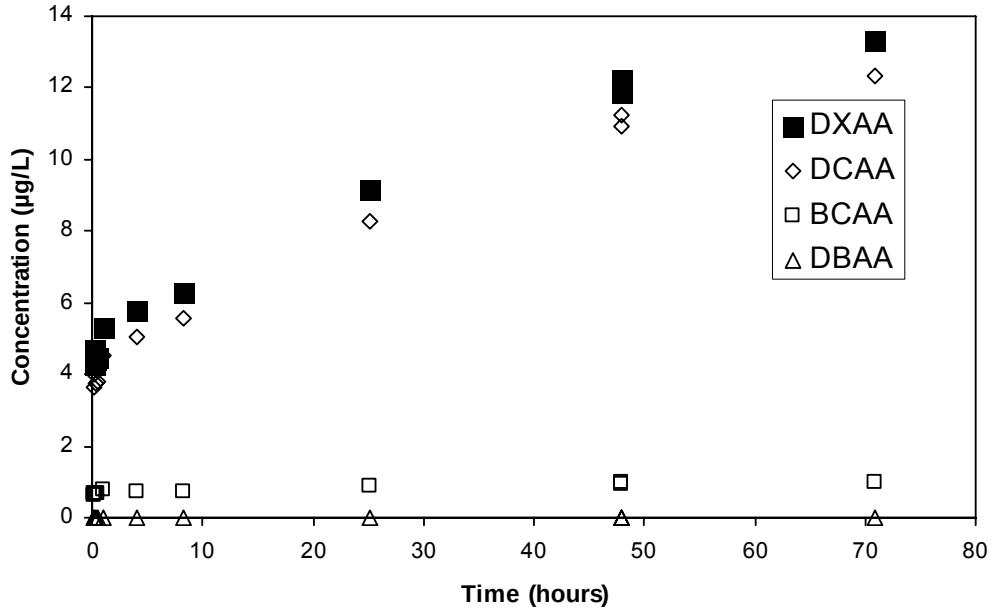


Figure 5-1 – DXAA formation kinetics in Metedeconk River water during chloramination at pH 8

5.3.1. Effect of Bromide Concentration

DXAA speciation is of interest because the health effects of bromine-substituted HAAs may be of more concern (Bull *et al.,* 1995; Karagalioglu *et al.,* 2000; Karagalioglu *et al.,* 2002). In this research, the factor n_D' is used to characterize the degree of bromine substitution of DXAAs. The value of n_D' can range from zero (all DCAA) to two (all DBAA). Lake Austin source water, for example, had a higher n_D' than Metedeconk River after 72 hours (0.5 vs. 0.06) because of its higher ambient bromide concentration (168 µg/L) and Br^-/DOC ratio (45 µg/mg). Charleston source water had higher ambient bromide (183 µg/L) and DOC concentrations (5.11 mg/L), but a lower Br^-/DOC ratio (36

μg/mg) and n_D' (0.23) than Lake Austin source water. The lower n_D' may be attributed to the lower Br^-/DOC ratio.

The effect of bromide concentration on DXAA formation and speciation during chloramination was investigated further by spiking Metedeconk River source water with 0.5 mg/L of bromide (Figure 5-2). The addition of bromide caused both a 35% increase in DXAA formation, 18 μg/L compared to 13 μg/L after a 72-hour incubation period, and a shift in speciation to the bromine-substituted species; the source water spiked with bromide formed less DCAA and more BCAA and DBAA than the source incubated at the ambient bromide concentration (Figure 5-1). However, when these data were analyzed on a molar basis (Figure 5-3), a smaller increase in HAA formation (16%) was observed in the bromide-spiked water. The discrepancy between the mass and molar analyses is explained by variations in speciation (bromine-substituted species weigh more than their chlorine-substituted counterparts). Therefore, HAA formation in Metedeconk River source water in the presence of a bromide spike (0.5 mg/L) mainly caused an increase in bromine incorporation without significantly increasing the molar yield. Hwang *et al*. (2000) observed a similar response in Colorado River water NOM fractions. Symons *et al*. (1998) observed that the addition of bromide did not have a large effect on the HAA_6 concentration in Lake Houston water, but significantly increased HAA_6 concentrations in California State Project water. The Br^-/DOC ratio is a way of normalizing the bromide concentration among various water sources and more accurately reflects the potential for forming bromine-substituted DXAAs than does the bromide concentration alone. Very high Br^-/DOC ratios (i.e., those achieved in laboratory studies by spiking waters with high amounts of bromide) may increase DXAA molar yield, but small effects should be observed over the typical range encountered in practice.

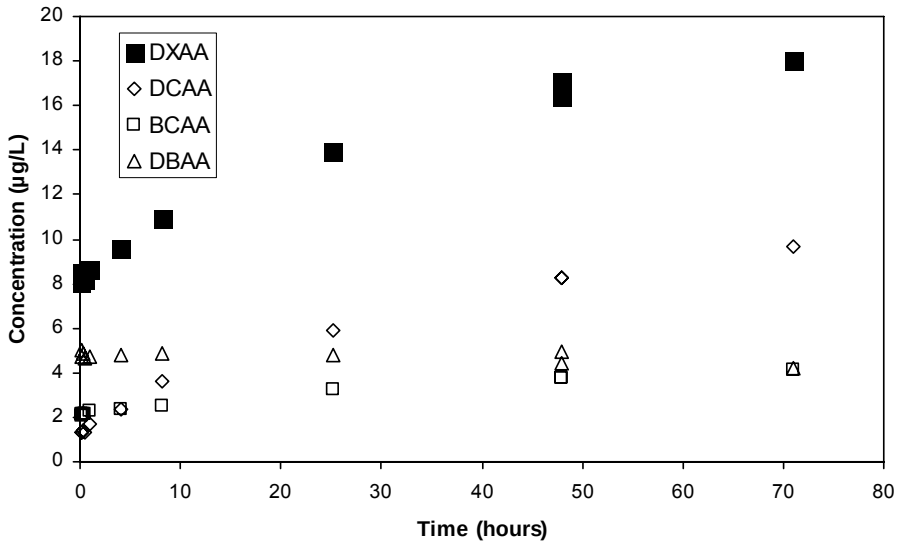


Figure 5-2 – DXAA formation kinetics in Metedeconk River source water during chloramination with 0.5 mg/L bromide addition at pH 8

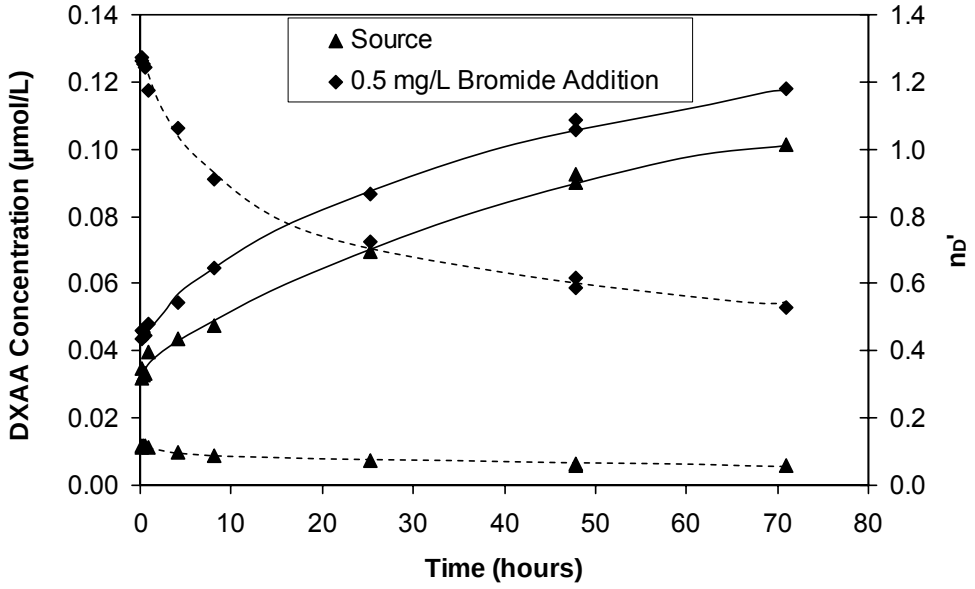


Figure 5-3 – DXAA formation kinetics and bromine incorporation ratio (n_D') in Metedeconk River source and source with 0.5 mg/L bromide addition at pH 8 (Solid lines represent DXAA concentration and dashed lines represent n_D')

The relative kinetics of each species is also shown in Figure 5-2. The bromine-substituted species (BCAA and DBAA) formed very rapidly, whereas the DCAA formation kinetics was characterized by an initial fast period of formation followed by a period of slower formation. Only about 14% of the 72-hour DCAA concentration formed after 5 minutes in the source water in the presence of a bromide spike, whereas 50% of the 72-hour BCAA concentration formed after 5 minutes and the DBAA essentially formed almost immediately in this water (*i.e.*, in <5 minutes). This trend in speciation is also apparent in the investigation of the bromine incorporation ratio (Figure 5-3). As expected, n_D' decreased over time because of the relative kinetics of each species. Bousher *et al*. (1989) and Vikesland *et al.* (2001) determined that two rate limiting reactions may be important when bromide is oxidized in the presence of monochloramine. The bromide present can react with free chlorine produced by monochloramine hydrolysis (Reaction 1) to form hypobromous acid (Reaction 2) or with the monochlorammonium ion (Reaction 3) to produce monobromamine (Reactions 4 and 5).

$$NH_2Cl + H_2O \rightarrow NH_3 + HOCl \quad (1)$$

$$HOCl + Br^- \rightarrow HOBr + Cl^- \quad (2)$$

$$NH_2Cl + H^+ \leftrightarrow NH_3Cl^+ \quad (3)$$

$$NH_3Cl^+ + Br^- \rightarrow NH_3Br^+ + Cl^- \quad (4)$$

$$NH_3Br^+ \leftrightarrow NH_2Br + H^+ \quad (5)$$

$$NH_3Br^+ + NH_2Cl \rightarrow NHClBr + NH_4^+ \quad (6)$$

$$HOBr + NH_2Cl \rightarrow NHClBr + H_2O \quad (7)$$

During chloramination, bromide oxidation by monochloramonium ion usually dominates, and once hypobromous acid and monobromamine are formed, they undergo further rapid reactions to produce chlorobromamines (Reactions 6 and 7), primarily

chlorobromamine, which is a very reactive brominating agent (Valentine 1986; Vikesland *et al.,* 2001). Therefore, the observed shift in DXAA speciation, the relative formation kinetics of each DXAA species, and the occasional overall molar increase in HAA formation likely occur because of the relatively higher reactivity of the bromine-substituted reactive species as compared to their chlorine-substituted counterparts.

5.3.2. Effect of pH

The impact of pH on DXAA formation kinetics was also investigated because pH significantly influences DXAA formation (Diehl *et al.,* 2000). Lake Austin source water incubated at pH 7 exhibited greater DXAA formation than that at pH 9 (Figure 5-4). Both pH values had a fast period of formation followed by a slower period. Over the first 30 minutes, each water formed similar concentrations of DXAA, Thereafter, more rapid kinetics were observed in the water incubated at pH 7, with greater concentrations of each individual species relative to pH 9. The pH affected both the kinetics and the extent of formation of each species. The effect was most apparent in the bromine-substituted DXAA species. The formation of both BCAA and DBAA over the first 30 minutes was independent of pH; however, after this initial period of formation, more rapid kinetics were observed in the water incubated at pH 7. After the first 30 minutes, the BCAA formation rate was approximately 0.15 μg/L-day at pH 9 versus 0.75 μg/L-day at pH 7, while the DBAA formation rate was essentially zero at pH 9 versus almost 0.5 μg/L-day at pH 7. DCAA formation was also affected by pH; significantly more rapid kinetics were observed in the water incubated at pH 7 over the first 8 hours. Thereafter, DCAA formation rates were similar; an additional 0.70 μg/L-day formed at pH 7 while 0.56 μg/L-day formed at pH 9.

In Metedeconk River source water (Figure 5-5), concentrations of DXAA similar to those found in Lake Austin water were formed during the first 30 minutes. Thereafter,

more rapid kinetics were observed in the water incubated at pH 7.2, relative to pH 9. However, unlike Lake Austin source water, BCAA formation was essentially the same at pH 7 and 9. The absence of a pH effect of on bromine-substituted HAA formation in this water is likely due to its low ambient bromide concentration. The Metedeconk River source water had a significantly lower ambient bromide concentration (approximately 30 μg/L) compared with Lake Austin (approximately 170 μg/L). Less DXAA formation was observed at pH 7 (Figure 5-5) than at pH 8 (Figure 5-2), which was unexpected because previous experiments with Metedeconk River source resulted in greater DXAA formation at pH 7 than at pH 8 (Figure 4-5). However, the results presented in (Figure 5-5) were obtained from a different batch of Metedeconk River source water, which had a lower DOC concentration (3.0 mg/L) than used for the rest of the experiments in this chapter. When analyzed on a yield basis, similar results were obtained at pH 7 and 8. Therefore, these results also illustrate the significant role water quality characteristics play in DXAA formation.

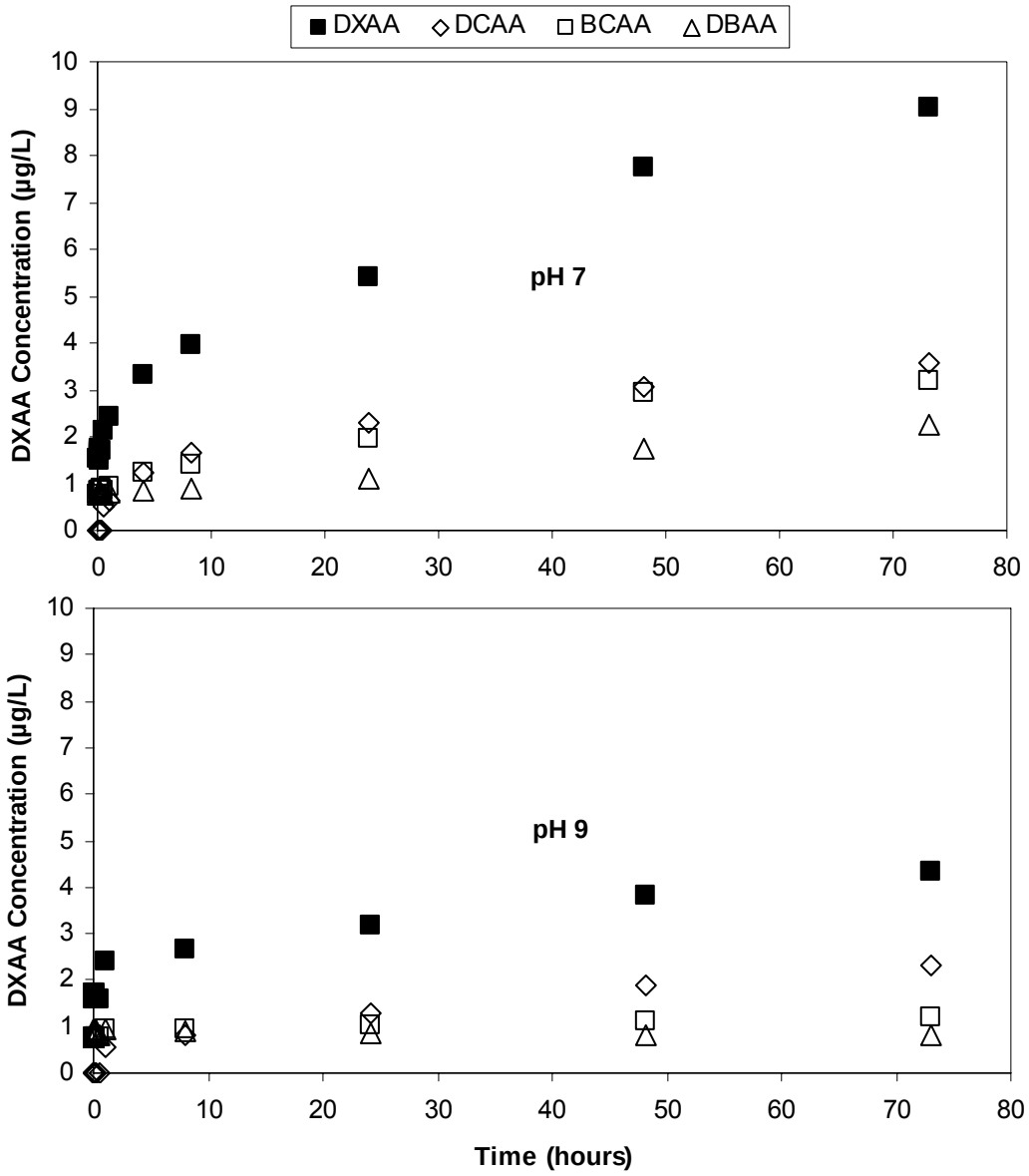


Figure 5-4 – Effect of pH on DXAA formation in Lake Austin source water

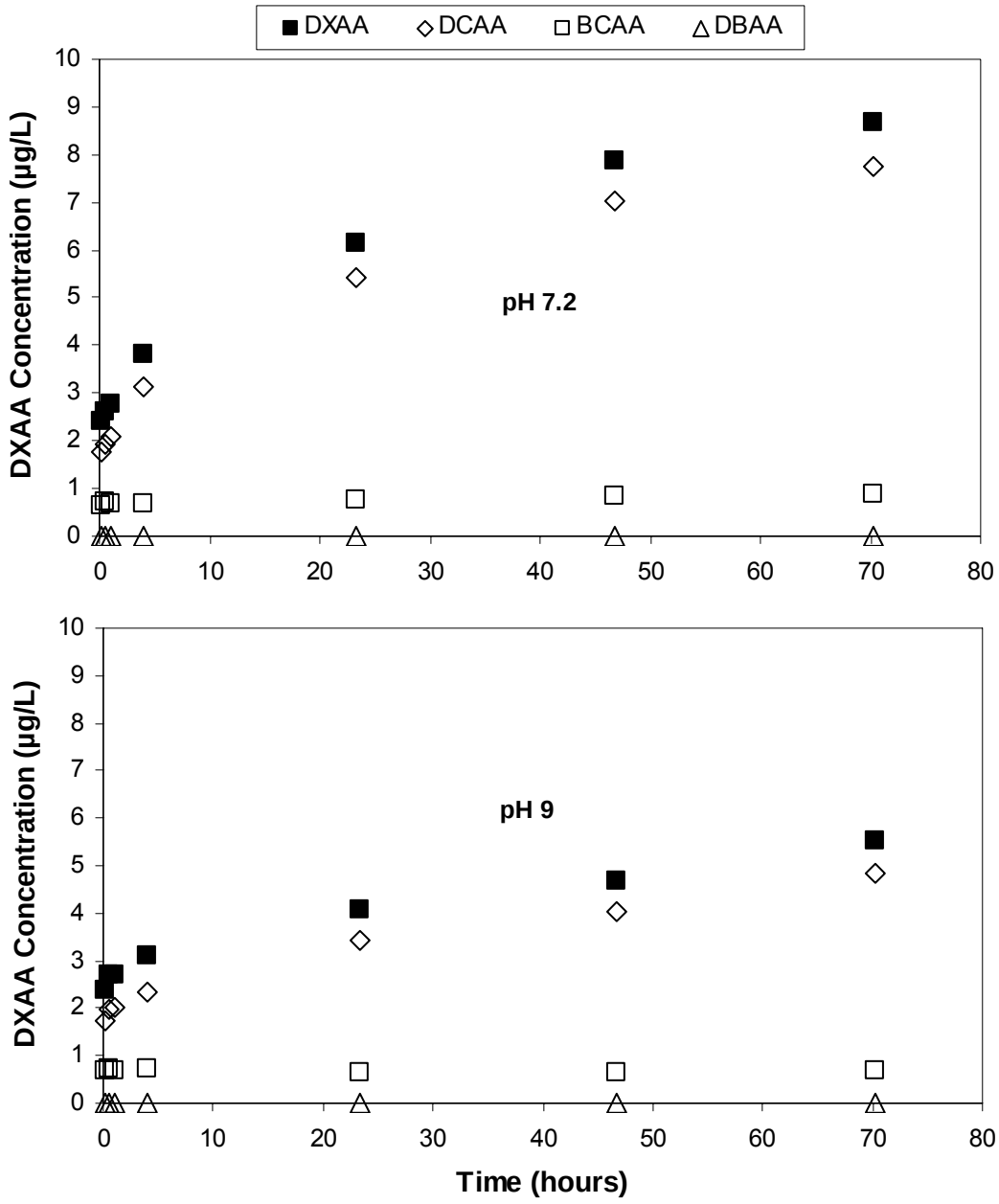


Figure 5-5 – Effect of pH on DXAA formation in Metedeconk River source water

The general trend of increased HAA formation at lower pH indicates that acid catalyzed monochloramine, monobromamine, and bromochloramine reactions may be responsible. NOM reactions with increased concentrations of one or more of several

reactive species (dichloramine, dibromamine, bromochloramine, free chlorine, free bromine, monochlorammonium ion, and monobromammonium ion) are the likely cause of increased DXAA formation as the pH decreased. The overall rate of chloramine decomposition is primarily limited by the rate of formation of dichloramine, which then rapidly decomposes (Jafvert and Valentine 1992). Dichloramine formation occurs in two ways, through monochloramine hydrolysis (Reaction 1) and the subsequent monochloramine reaction with free chlorine (Reaction 8), and through monochloramine disproportionation (Reaction 9). Reaction 9 is general acid catalyzed, and a variety of proton donating species (general acid catalysts such as the acid forms of carbonate, phosphate, and sulfate, as well as acetic acid) can act to accelerate monochloramine decay (Vikesland *et al.,* 2001).

$$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O \quad (8)$$

$$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3 \quad (9)$$

Therefore, when the solution pH is decreased, the rate of monochloramine loss is increased. This accelerated decay is due to the enhanced rate of dichloramine formation at lower pH. In experiments with Lake Austin and Lake Houston source water, Diehl (2001) observed that the formation of HAAs increased under conditions favorable for the presence of dichloramine. Therefore, dichloramine or its resultant decomposition products (e.g., free chlorine) may be the active halogenating agent. Monochlorammonium ion (Reaction 3) is another possible halogenating species. This reaction has a pK_a of 1.5, indicating that any reaction involving NH_3Cl^+ in natural waters can be expressed as an acid catalyzed reaction of NH_2Cl (Jafvert and Valentine 1992). Symons *et al*. (1998) postulated that NH_3Cl^+ may be an active halogenating agent that plays in increasingly important role as the pH decreases.

Bromamine chemistry has considerable similarity with chloramine chemistry. Lei *et al*. (2004) has shown that the monobromamine disproportionation reaction (Reaction 10) is also general acid catalyzed. Chlorine is a better oxidant than bromine, but bromine is a better nucleophile than chlorine. As a result, bromamines decay faster than chloramines. Therefore, dibromamine, or its resultant degradation products, may also be an active halogenating agent resulting in increased bromine-substituted DXAA formation as the pH is decreased. In addition, monobromamonium ion (NH_3Br^+), formed in a reaction analogous to Reaction 3, may also be an active halogenating agent.

$$NH_2Br + NH_2Br \rightarrow NHBr_2 + NH_3 \qquad (10)$$

Others (Trofe *et al*., 1980; Vikesland 1986; Bousher *et al*., 1989; Gazda and Margerum 1994) have shown that bromochloramine can also form in solutions that contain monochloramine and bromide. This mixed haloamine may also be of increased importance as the pH decreases because its formation is dependent upon pH; increasing as the pH decreases.

In addition to haloamine speciation, pH can also affect the 3-D structure of NOM molecules. At low pH, the carboxylic and phenolic functional groups of the NOM are more neutralized, decreasing the electrostatic repulsion between adjacent functional groups and causing the NOM molecule to coil (Ghosh and Schnitzer 1980; Murphy *et al.*, 1994). This change in structure may influence the reactivity of the NOM.

5.3.3. Effect of Treatment

Treatment processes can affect the rate and extent of HAA formation through removal of DOC, alteration of DOC reactivity, and changes in the Br^-/DOC ratio. The effect of coagulation or softening on DOC removal and 72-hour DXAA formation is illustrated in Figure 5-6. The waters undergoing alum coagulation (Charleston and Metedeconk River) exhibited over a 50% decrease in DXAA concentration relative to

their respective source waters. This considerable decrease is attributed to the significant DOC removal (~50%) attained by coagulation, which also decreased the SUVA by greater than 54%. Softening Lake Austin and Biscayne Aquifer source water had a minimal effect on reducing DXAA formation when compared to the coagulated Metedeconk River and Charleston source waters. This relative difference can be related to the smaller degree of organic carbon removal in the softened waters. The influence of treatment on DXAA reaction rates were also examined. Even in the softened waters where a less significant degree of DOC removal was achieved, treatment decreased the initial rate of DXAA formation observed in the first hour. However, neither coagulation nor softening had a significant influence on the rate of DXAA formation after the initial period of fast formation.

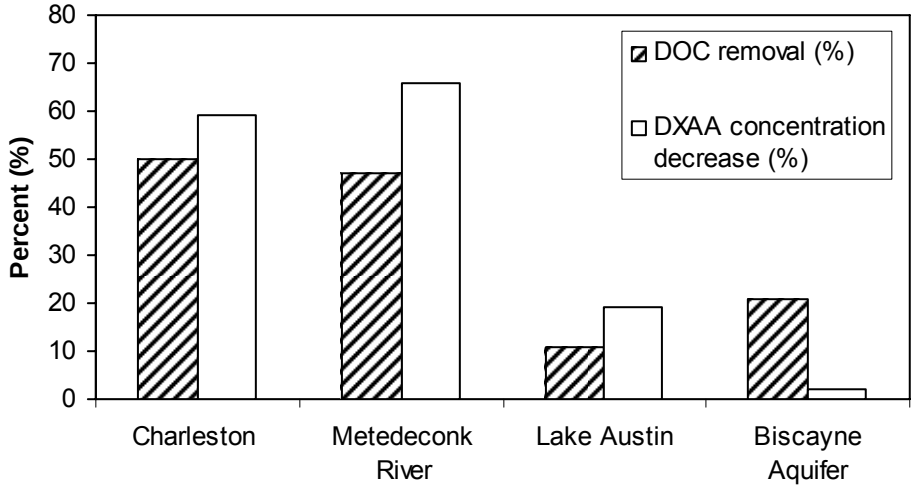


Figure 5-6 – Effect of coagulation (Charleston and Metedeconk River) or softening (Lake Austin and Biscayne Aquifer) on DOC removal and DXAA formation (all waters incubated 72 hours except Biscayne Aquifer, which was incubated 48 hours)

Both the reactivity and the concentration of the organic carbon in waters can influence HAA formation. To determine if observed differences in DXAA formation

were truly related to differing reactivity, or just a reflection of DOC concentration, DXAA yields were examined (Figure 5-7). The 72-hour DXAA mass yields in the coagulated waters (Charleston and Metedeconk River) were approximately 75% of the yield in source water. Thus, coagulation preferentially removed the more reactive fraction of NOM, which is further supported by the 54% decrease in SUVA observed in both waters. Softening of the Lake Austin and Biscayne Aquifer source waters had a relatively small effect on DXAA yield. The reactivity of Lake Austin water decreased slightly, while that Biscayne Aquifer increased somewhat. In addition, softening did not have a significant influence on the initial normalized DXAA reaction rate (DXAA yield/time). However, coagulation did decrease the initial normalized reaction rate, which is substantiated by the preferential removal of SUVA attained.

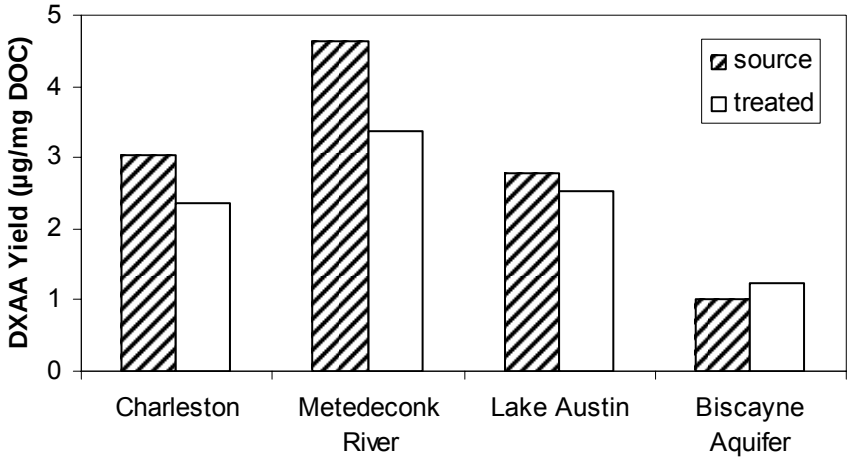


Figure 5-7 – Effect of treatment on DXAA Formation (Charleston and Metedeconk River incubated at pH 8, source waters were coagulated; Lake Austin and Biscayne Aquifer incubated at pH 9, source waters were softened; all waters incubated 72 hours except Biscayne Aquifer, which was incubated 48 hours)

Coagulation of Metedeconk River and Charleston source waters removed approximately 50% of the DOC, thereby increasing the Br^-/DOC ratios and DXAA

bromine incorporation. In contrast, softening of Lake Austin and Biscayne Aquifer water only removed a small amount of organic carbon and did not significantly increase the Br^-/DOC ratio. As a result, softening had minimal influence on the degree of bromine incorporation. Changes in the Br^-/DOC ratio potentially can have significant kinetic implications, because of the faster formation kinetics of the bromine-substituted DXAA species noted above.

5.4. PRECHLORINATION

The impact of prechlorination on DXAA formation is important because many utilities have a period of free chlorination prior to ammonia addition to achieve CT requirements. Three different waters (Metedeconk River coagulated, Lake Austin source, and Biscayne Aquifer softened) were used to study the impact of prechlorination on DXAA formation. The type of water studied (*i.e.*, treated or source) corresponded to the type of water that is prechlorinated at the actual drinking water treatment plants. Prechlorination increased DXAA formation as well as formation of mono- and tri-halogenated acetic acids. The relative effects of prechlorination on DXAA formation were similar in all of the waters studied (Figure 5-8). In Lake Austin source water, for example, chloramination resulted in only 9 µg/L DXAA after 48 hours, while prechlorinating for 5 and 20 minutes formed 25 µg/L and 35 µg/L of DXAA, respectively. Also, as expected, the longer the period of free chlorination the greater the DXAA formation; however, the increase was much less than proportional to the prechlorination time. In addition, a majority of the DXAA formation occurred during the prechlorination period. At least 75% of the 72-hour DXAA concentration formed during prechlorination in all the waters studied. Typically, however, greater than 90% of the DXAA formed during prechlorination. This indicates that even though prechlorination

caused increased DXAA formation, very little additional DXAA formed during the chloramination period.

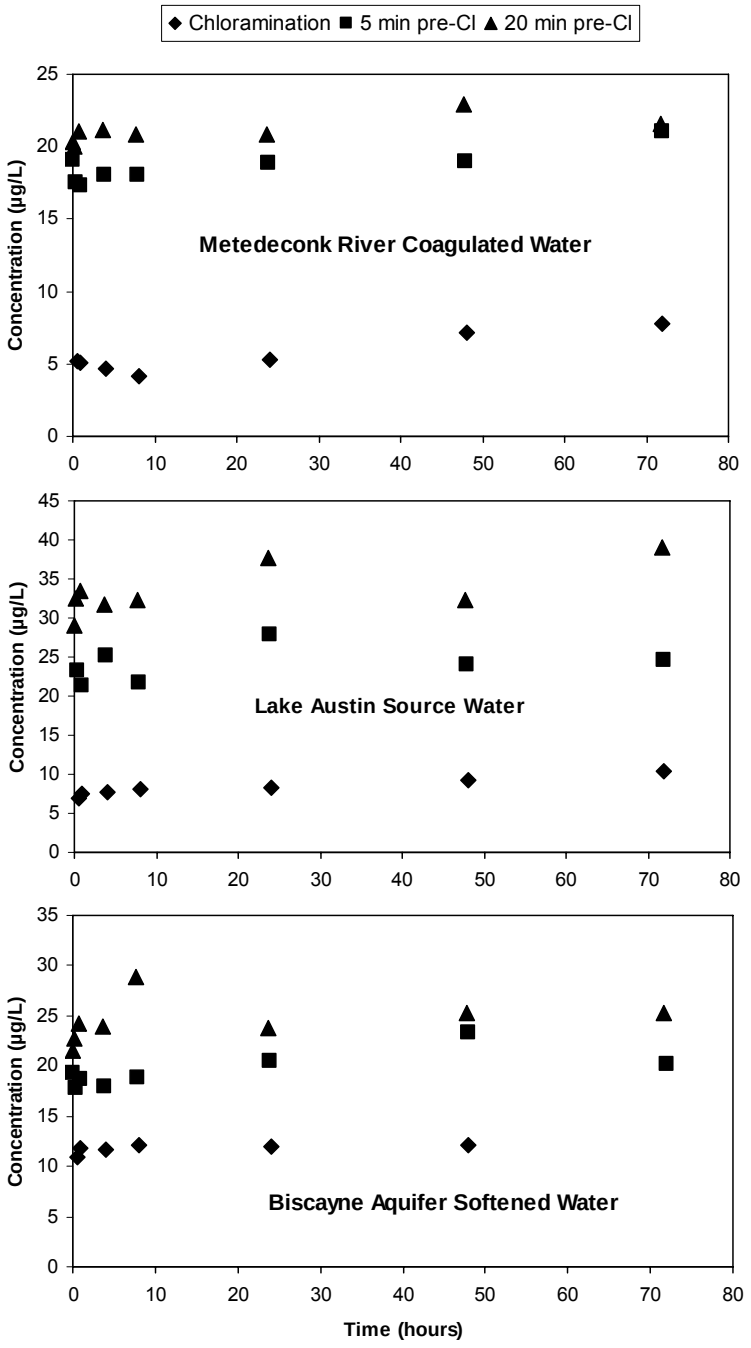


Figure 5-8 – Effect of prechlorination on DXAA formation kinetics (time zero corresponds with start of chloramination)

The DXAA formation during the chloramination period was examined in greater detail by subtracting the formation as a result of prechlorination from the total DXAA concentration at each time interval (Figure 5-9). Again, the trends were similar in all three water sources. Prechlorination of Metedeconk River coagulated and Biscayne Aquifer softened waters resulted in essentially no additional DXAA formation after ammonia addition. The Lake Austin source water data, however, were more scattered and had some outliers, yet still minimal additional DXAA formation occurred during the chloramination period. These results indicate that, during the prechlorination period, free chlorine reacts with most of the fast reactive NOM sites; therefore, after subsequent ammonia addition and chloramine formation very little additional DXAA is formed. This is of practical significance to plants that prechlorinate as it indicates that most all of the HAAs form during the chlorination step. These results also suggest that both chlorine and monochloramine (or monochloramonium ion) react with the same fraction of the NOM to produce DXAAs, or that the DXAAs formed during chloramination do so as a result of the HOCl that is formed by monochloramine hydrolysis.

Prechlorination may also increase the formation of bromine-substituted HAAs. Cowman and Singer (1996) noted that the extent of bromine incorporation was greater during chlorination as compared to chloramination. Free chlorine reacts with bromide to form HOBr, which attacks more NOM sites faster than HOCl does, thus leading to more bromine incorporation as the ambient Br^- concentration increases. The influence of prechlorination on bromine incorporation into HAA_9 is shown in Figure 5-10. In general, prechlorination resulted in greater bromine incorporation than chloramination alone, and the longer the prechlorination period the greater the bromine incorporation. The increased bromine substitution may result from the increased concentration of HOBr

present during prechlorination, which is only present in small concentrations during chloramination.

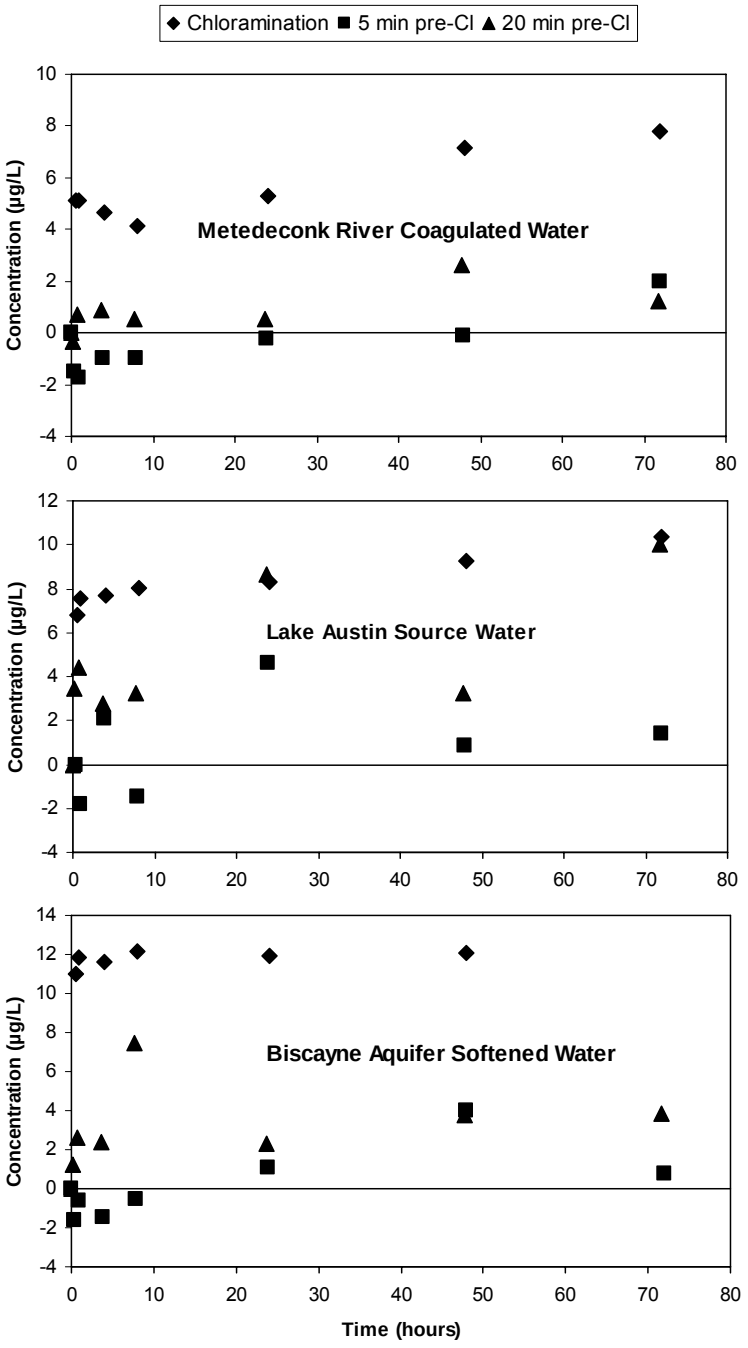


Figure 5-9 – DXAA formation during the period of chloramination only (DXAA formed during chloramination = total DXAA – DXAA formed during prechlorination)

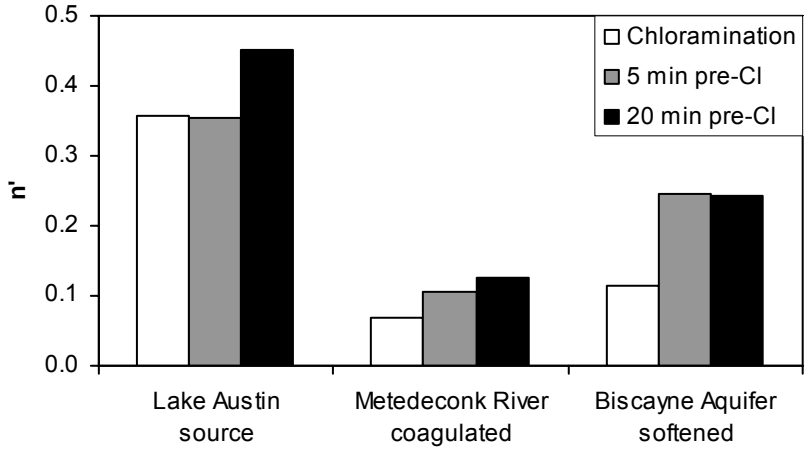


Figure 5-10 – Effect of prechlorination on HAA_9 speciation (72-hour incubation)

Chloramination typically produces negligible THM formation, whereas periods of free chlorination cause THMs to form. The influence of prechlorination on THM formation is shown in Figure 5-11. The longer the period of free chlorination the greater the THM formation, and in both Lake Austin and Biscayne Aquifer waters, once the prechlorination period was complete (ammonia was added and chloramines formed) minimal THM formation occurred. In contrast, quenching the prechlorination period with ammonia did not limit the THM formation as effectively in coagulated Metedeconk River water; THM concentrations doubled between the prechlorination periods of either 5 or 20 minutes and 72 hours. However, the total THM concentrations after 72 hours were only 15 and 23 μg/L for the 5 and 20 minute prechlorination periods, respectively. The additional THM formation in coagulated Metedeconk River water may be linked either to its NOM characteristics (Metedeconk River source water was significantly more reactive than the other source waters studied with respect to HAA_9 yield under chlorination UFC) or to water quality characteristics that affect the concentration of the reactive halogenating species. In addition, the different treatment conditions, specifically the pH

that each water was subjected to (Metedeconk River coagulated water was incubated at pH 8, while Lake Austin source and Biscayne Aquifer softened waters were incubated at pH 9), may have influenced THM formation patterns.

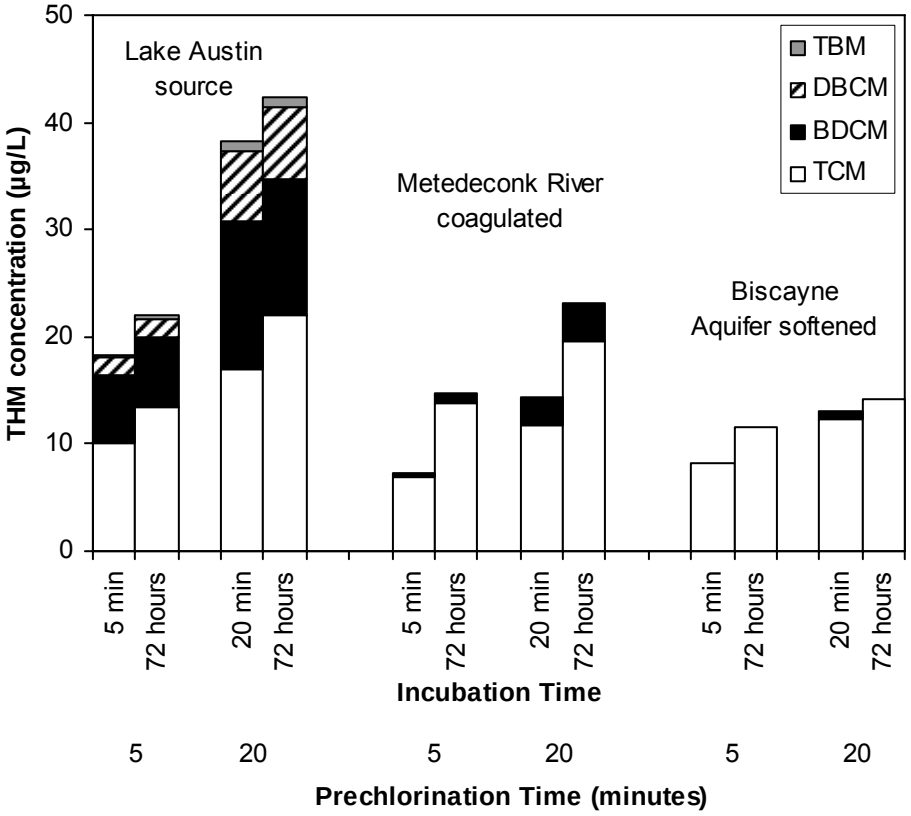


Figure 5-11 – Effect of prechlorination on THM formation

5.5. DAVIS DWTP (LAKE AUSTIN) AND DISTRIBUTION SYSTEM

The Davis Drinking Water Treatment Plant and associated distribution system were sampled to confirm the HAA formation kinetics measured in the laboratory. This plant chlorinates Lake Austin source water for approximately 6 minutes prior to ammonia addition and softening. Free chlorine was added to the pH 7.7 source water to produce a free chlorine residual of 0.8 mg/L. Then, chlorine, ammonia, and lime were added during rapid mix to produce a combined chlorine residual of approximately 2.2 mg/L at about a

4/1 Cl_2/N ratio. This converted the free chlorine to chloramines and softened the water, which increased the pH to greater than 9. Samples were taken from the plant immediately before ammonia addition, after rapid mixing (ammonia and lime addition), after settling, and after filtration. The distribution system was also sampled at three different points that provided approximate residence times of 1.1, 2.4, and 3.1 days. The DXAA formation in the Davis DWTP and distribution system is illustrated in Figure 5-12. A majority of the DXAA formation occurred during the period of free chlorination with minimal additional formation occurring after ammonia was added to form chloramines. In fact, all DXAA formation occurred within the treatment plant itself, indicating that HAA control strategies should be focused on the chlorination step in plants that prechlorinate prior to chloramination.

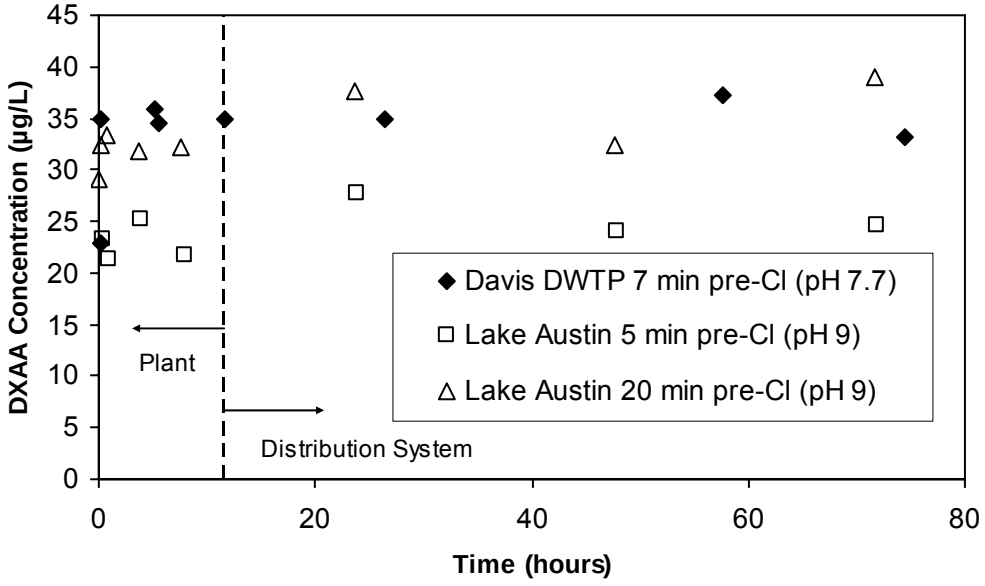


Figure 5-12 – DXAA formation in the Davis DWTP and distribution system

The Lake Austin source batch kinetic laboratory data are also shown in Figure 5-12. The trends in DXAA formation of the laboratory data parallel the formation at the

drinking water treatment plant. However, the DXAA formation at the Davis DWTP was greater than the formation observed in the laboratory. This discrepancy was due to differences in pH during prechlorination between the batch tests and plant operating conditions. Carlson and Hardy (1998) determined that response of HAA_5 formation at short contact times was arbitrary and site-specific, but observed that the pH of maximum HAA formation ranged from 6.5 to 7.5 depending on the water source. Therefore, the laboratory experiments may have formed less DXAA because they were conducted at pH 9, while prechlorination at the treatment plant occurred at pH 7.7.

Chloramination limits the formation of mono-and tri-halogentated HAAs (MXAAs and TXAAs, respectively), predominantly forming DXAAs. In the absence of prechlorination, DXAAs typically accounted for approximately 90% of the HAA_9 formation. Even brief periods of prechlorination, however, may cause significant concentrations of MXAAs and TXAAs to form as well. The HAA_9 formation at the Davis water treatment plant is shown in Figure 5-13. DXAAs were the predominant species formed, accounting for approximately 60% of the total HAA_9 formation; however, significant concentrations of TXAAs and some MXAAs also formed. Prechlorination, therefore, increased the formation of the other regulated HAA species, forming approximately 60 µg/L of HAA_9 and almost 47 µg/L of HAA_5 (regulated at 60 µg/L). Again, as with the DXAAs, almost all of the formation occurred in the prechlorination step, and the species remained stable throughout the treatment plant and distribution system, which is expected as the high pH (9.4) discourages biodegradation of HAAs in the distribution system.

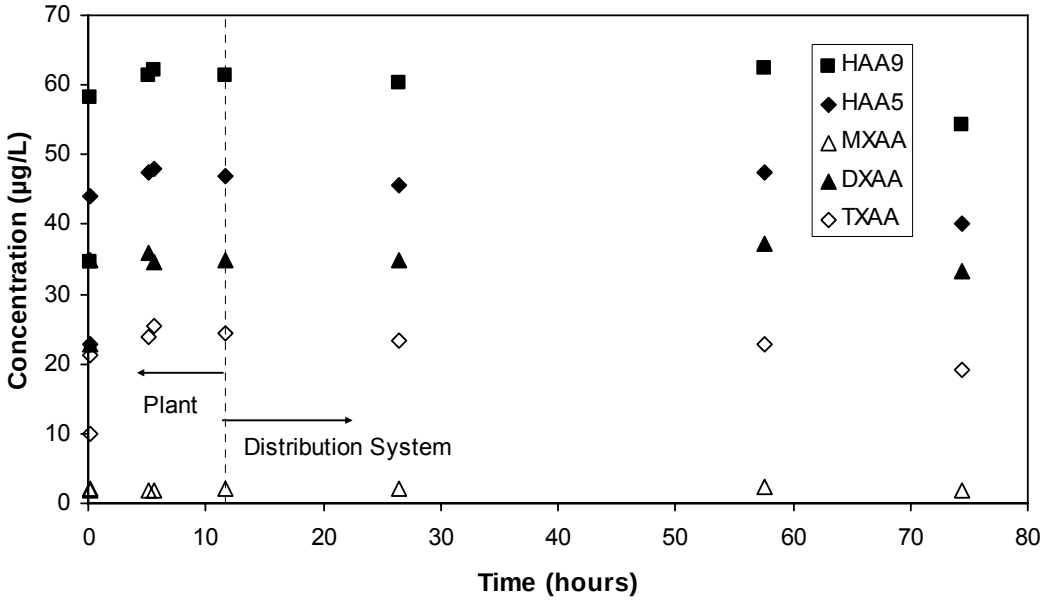


Figure 5-13 – Total HAA formation in the Davis DWTP and distribution system

5.6. SUMMARY

The kinetics of DXAA formation during chloramination are characterized by an initial rapid period of formation followed by a period of slower formation, and the bromine-substituted species (BCAA and DBAA) form more rapidly than DCAA. The pH also had a significant influence on DXAA formation. More rapid DXAA formation kinetics were observed at pH 7 than at pH 9. The initial rapid period of formation (i.e. <30 minutes) was independent of pH; however, after 30 minutes, more rapid kinetics were observed at lower pH. This pH trend indicates that acid catalyzed monochloramine, monobromamine, and bromochloramine reactions may be the cause of increased HAA formation as the pH decreases.

The effectiveness of treatment on DXAA formation is largely related to DOC removal, although preferential removal of the more reactive NOM fractions may also contribute to reduced DXAA formation. The effect can be seen in two ways: decreased DXAA formation during the initial period of rapid formation, and increased bromine incorporation through the resulting increase in the Br^-/DOC ratio. Treatment did not, however, have a significant impact on DXAA formation rates after the initial period of rapid formation.

During short periods of prechlorination (5 or 20 minutes), significantly more DXAA formation, as well as formation of mono- and tri-halogenated acetic acids, occurred relative to chloramination alone. During the prechlorination period, free chlorine reacts with most of the fast-reactive NOM sites. As a result, after subsequent ammonia addition and chloramine formation very little additional DXAA is formed. Therefore, the general expectation is that very little of the DXAA formation in chlorination/chloramination plants is associated with the chloramination step, despite the dramatic difference in the chloramine and chlorine contact times that is typical of such plants. Thus, HAA control strategies should be focused on the chlorination step in plants that prechlorinate prior to chloramination. The absence of significant DXAA formation during chloramination after prechlorination suggests that both chlorine and monochloramine (or monochloramonium ion) react with the same fraction of the NOM to produce DXAAs, or that the DXAAs formed during chloramination do so as a result of the HOCl that is formed by monochloramine hydrolysis.

CHAPTER 6: Haloamine Reactivity

6.1. INTRODUCTION

When bromide is present in source water, bromine-substituted haloacetic acids typically form during chloramination. Limiting the formation of bromine-substituted HAAs is of particular interest because recent studies have shown that they may pose a greater health risk than their chlorine-substituted counterparts (Bull *et al.,* 1995; Karagalioglu *et al.,* 2000; Karagalioglu *et al.,* 2002). Monochloramine is the dominant haloamine species under drinking water treatment conditions. In the presence of bromide, however, bromine-substituted haloamines, such as mono- and dibromamine, as well as bromochloramine may also form. Even though these species are present in significantly lower concentrations that monochloramine, they may be significantly more reactive. Therefore, increased knowledge of the reactivity of bromine-substituted haloamines is necessary to understanding HAA formation in waters that contain bromide.

6.2. BROMAMINE REACTIVITY

The reactivity of different haloamine species was studied under controlled conditions in two natural waters of differing characteristics, Lake Austin, TX and Metedeconk River, NJ. The water quality characteristics for each of these waters are shown in Table 6-1. Lake Austin water is a low specific ultraviolet absorbance (SUVA), high bromide, hard, high alkalinity source water, while Metedeconk River water is characterized as a moderately high SUVA, low bromide source water. These source waters were selected not only because of their different characteristics, but also to provide consistency with previous the studies in this research.

Table 6-1 – Typical source water quality characteristics

Parameter	Lake Austin source	Metedeconk River source
pH	8.1	6.7
TOC (mg/L)	3.55	3.25
DOC (mg/L)	3.45	3.01
Alkalinity (mg $CaCO_3$/L)	150	14
SUVA (L/mg-m)	2.11	4.87
Bromide (µg/L)	168	27

6.3. BROMAMINE REACTIVITY

Natural waters form Lake Austin and Metedeconk River were dosed with preformed bromamine stock solutions. The pH and Br_2/N ratio of these solutions were selected to provide dosing solutions containing predominantly mono- or dibromamine. Bromamine chemistry has been shown to be similar to that of the chloramines, and as with the chloramine system, bromamine reactions are also catalyzed by both phosphate and carbonate buffers (Lei *et al*., 2004). In light of this, only low phosphate buffer concentrations were used when necessary to minimize their influence on the reactions of interest. Bromamine doses were selected to provide a target residual concentration between 0.5 and 1 mg/L as Cl_2 at 24 hours. However, both bromamine residual and HAA_9 concentrations were measured at 48 and 72 hours to ensure the reaction conditions were NOM-limited.

6.3.1. Lake Austin source water

The bromamine reactivity experiments performed in Lake Austin source water are shown in Table 6-2. Experimental conditions were selected to determine the influence of small concentrations of phosphate buffer, pH, and Br_2/N ratio on HAA formation. The pH and Br_2/N ratio directly influenced which bromamine species predominated, allowing

their reactivities to be compared. This comparison was made by HAA yield, which is the HAA concentration normalized by the DOC concentration.

Table 6-2 – Summary of bromamine reactivity experiments in Lake Austin source water

pH	Br_2/N molar ratio	Phosphate Buffer (mM)	Initial Dose (mg Cl_2/L)	Initial Dose (NH_2Br; $NHBr_2$) (mM)
9	0.05	0	2.1	0.024; 0.003
9	0.05	0.18	2.0	0.022; 0.003
7.2	0.05	0.31	3.0	0.005; 0.019
7.2	0.667	0.33	1.9	0; 0.013

After 24 hours of incubation, each of the four experimental conditions resulted in similar HAA yield, and DBAA was the most predominant HAA formed (Figure 6-1). In addition, experiments show that bromamines are significantly more reactive than chloramines. After 24 hours of contact in Lake Austin source water (Figure 6-2), the bromamine species formed approximately four times the HAA_9 yield as the chloramines, indicating that the bromamine species are reactive enough to play a significant role in HAA formation in waters that contain bromide. Because each experiment was dosed with approximately 2 mg/L as Cl_2 of total bromamine, the reactivity of mono- and dibromamine could be compared. Each of these conditions resulted in similar HAA yields.

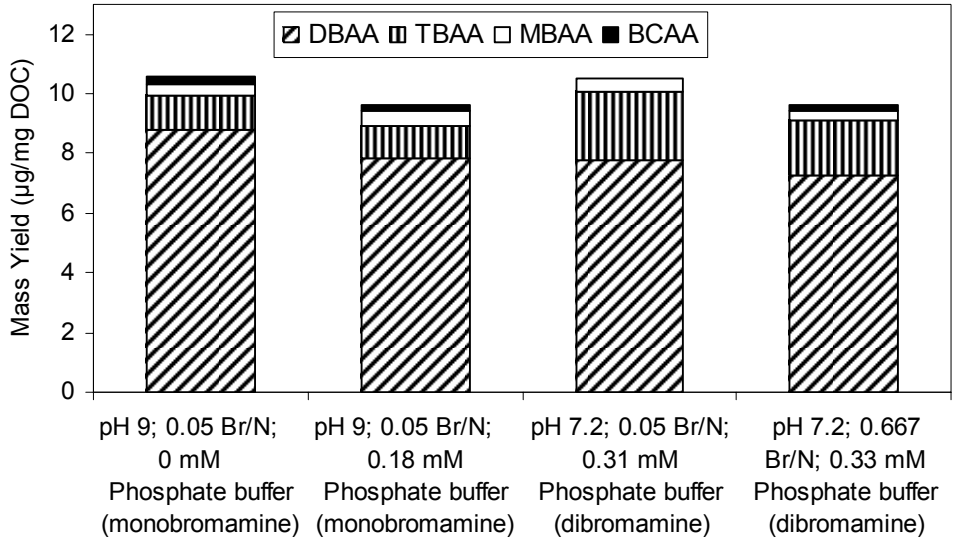


Figure 6-1 – HAA yield and speciation in Lake Austin source water after 24 hours incubation (parentheses indicate dominant bromamine present)

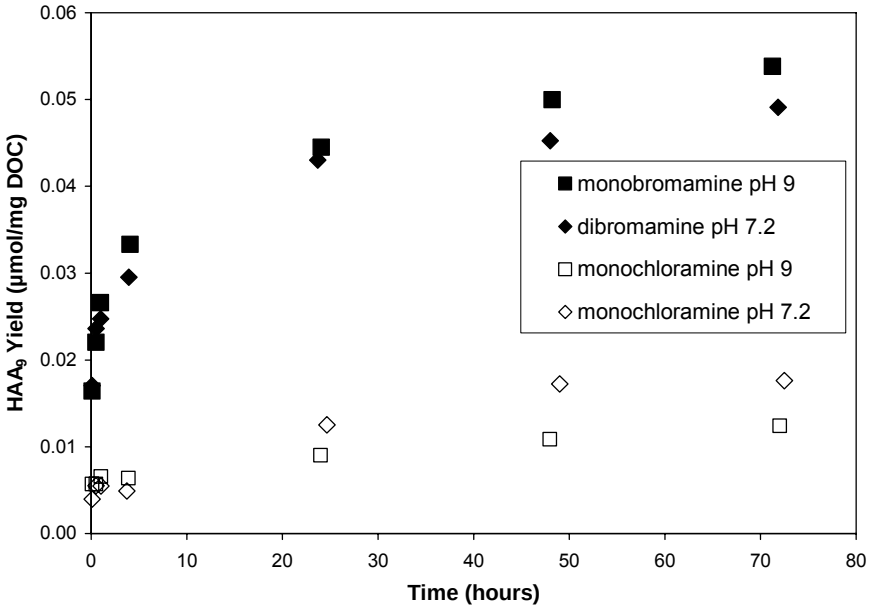


Figure 6-2 – Haloamine reactivity in Lake Austin source water (Experimental conditions: mombromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.022 mM, $NHBr_{2o}$ = 0.003 mM; dibromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.013 mM; monochloramine pH 9: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM; monochloramine pH 7.2: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM)

6.3.2. Metedeconk River source water

As with Lake Austin source water, Metedeconk River source water was dosed with different bromamine solutions formulated to produce predominantly mono- or dibromamine (Table 6-2). However, the bromamine decay rate in Metedeconk River was significantly greater than that of Lake Austin source water; therefore, higher initial doses were necessary to provide the target oxidant residual at 24 hours. In addition to the higher initial doses, waters were also spiked with additional bromamines at 48 hours to ensure that the HAA formation was NOM limited. The initial and 48-hour spike dose concentrations were selected to provide a total oxidant residual between 0.5 and 1 mg Cl_2/L at 24 and 72 hours, respectively.

Table 6-3 – Summary of bromamine reactivity experiments in Metedeconk River source water

pH	Br_2/N molar ratio	Phosphate Buffer (mM)	Initial Dose (mg Cl_2/L)	Initial Dose (NH_2Br; $NHBr_2$) (mM)
9	0.05	0	4.8	0.057; 0.005
9	0.05	0.40	5.0	0.056; 0.007
7.2	0.05	0.83	9.2	0.022; 0.054
7.2	0.667	1.43	9.0	0; 0.063

Similar to Lake Austin source water, after 24 hours the bromamines formed predominantly DBAA in Metedeconk River water source water (Figure 6-3). Metedeconk River water was also more reactive than Lake Austin water, which was not unexpected since it had a greater SUVA than Lake Austin (Table 6-1). Twenty-four hours after dosing, the bromamine species formed greater than 6 times the HAA_9 yield as the chloramines (Figure 6-4). Also, upon spiking the the Metedeconk River waters with

additional bromamines, very little additional HAAs formed, indicating that these experiments were most likely NOM limited.

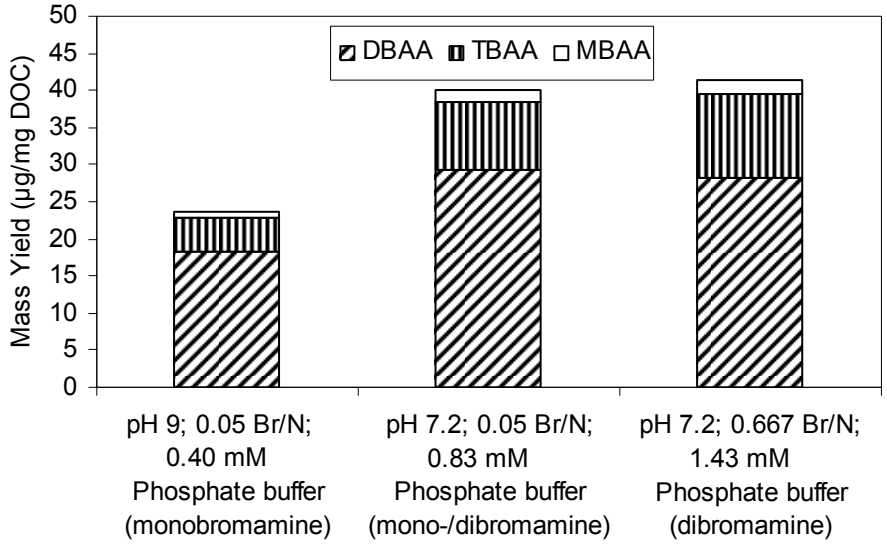


Figure 6-3 – HAA yield and speciation in Metedeconk River source water after 24 hours incubation (parenthesis indicate dominant haloamine present)

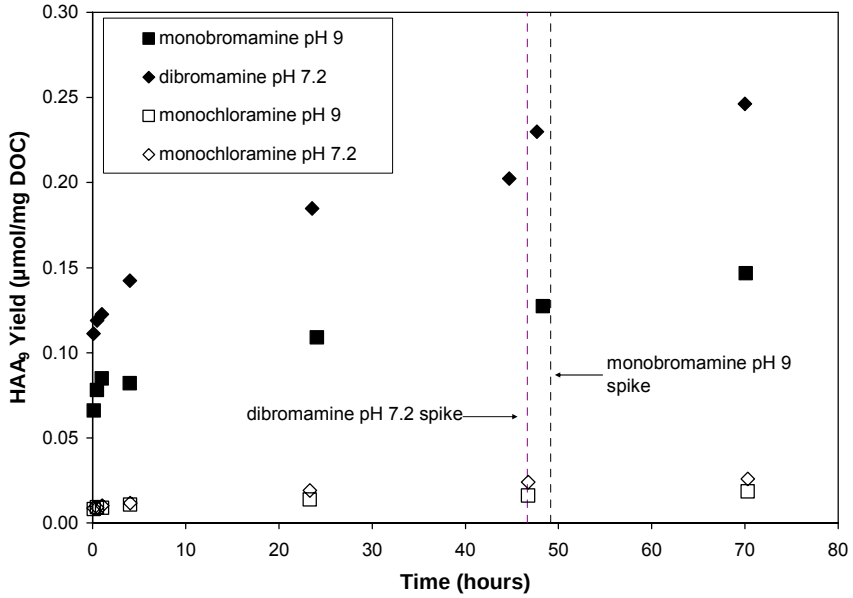


Figure 6-4 – Haloamine reactivity in Metedeconk River source water (Experimental conditions: Bromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.056 mM, $NHBr_{2o}$ = 0.007 mM; Bromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.063 mM; Chloramine pH 9: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM; Chloramine pH 7.2: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM; dashed line indicates time of additional bromamine spike)

Both the chloramines and bromamines formed predominantly DXAAs, and both resulted in an initial rapid period of HAA formation, followed by a slower period. Chloraminated source waters incubated at pH 7.2 exhibited greater DXAA formation than that at pH 9. From time zero until 30 minutes, similar concentrations of DXAA formed regardless of pH; however, after approximately 30 minutes more rapid kinetics were observed in the water incubated at pH 7.2. The increased HAA formation at lower pH indicates that acid catalyzed chloramine reactions may be responsible. Therefore, monochloramine decay products such as NH_3Cl^+, $NHCl_2$, HOCl may be the cause of the more rapid HAA formation at low pH after the initial 30 minutes of reaction. Lei *et al.* (2004) postulated that the reactions for bromamine decomposition are analogous to the

chloramines. Hence, monobromamine disproportionates into dibromamine (reaction 1), and dibromamine hydrolysis (reaction 2) may result in an unidentified reaction intermediate (I), which can react with $NHBr_2$ or NH_2Br (reactions 3 and 4) to form HOBr and various other products. Therefore, NH_2Br, $NHBr_2$, or HOBr may be responsible for the observed HAA formation.

$$2NH_2Br \leftrightarrow NHBr_2 + NH_3 \quad (1)$$

$$NHBr_2 + H_2O \rightarrow I \quad (2)$$

$$I + NHBr_2 \rightarrow HOBr + products \quad (3)$$

$$I + NH_2Br \rightarrow products \quad (4)$$

Greater concentrations of HOBr may form under conditions that promote the formation and decay of $NHBr_2$. The increased TBAA observed at pH 7.2 in comparison to pH 9, may be a result of either higher concentrations of $NHBr_2$ decomposition products, such as HOBr, or pH effects on NOM. At low pH, the carboxylic and phenolic functional groups of the NOM are more neutralized, decreasing the electrostatic repulsion between adjacent functional groups and causing the NOM molecule to coil (Ghosh and Schnitzer 1980; Murphy *et al.,* 1994). This change in structure may influence the reactivity of the NOM. However, Miller and Uden (1983) showed that the TCAA/DCAA ratio is dependent on chlorine dose and that higher HOCl favor TCAA formation. Therefore, if HOBr reactions with NOM are analogous to those of HOCl, the greater concentrations of HOBr that may be present at lower pH may be the cause of the observed increase in TBAA formation.

Metedeconk River source water, unlike Lake Austin, had greater HAA yields when dibromamine was the dominant bromamine species. This difference in reactivity may be a result of the NOM in Metedeconk River simply being more reactive, or that dibromamine is more reactive than monobromaine. In Metedeconk River, both

experiments were dosed with the same initial concentration of total bromamine (0.63mM). However, since one mole of dibromamine is equivalent to two moles of Cl_2, when compared on an equivalents basis, the monobromamine experiment at pH 9 was dosed with 5 mg/L as Cl_2, while the dibromamine experiment at pH 7.2 was dosed with 9 mg/L as Cl_2. Lake Austin source water was dosed with approximately 2 mg/L as Cl_2 of both mono- and dibromamine. Therefore, normalization of the HAA yield with haloamine dose, measured as equivalents of Cl_2, indicates that each of the bromamine species may be similar in reactivity, as seen in Lake Austin source water. Each of these experiments were thought to be NOM limited with respect to bromamine dose, especially at short reaction times. The dose, however, did have an impact on HAA formation (Figure 6-4). Therefore, the increased HAA formation observed in Meteconk River water dosed with dibromamine may be a result greater amounts of HOBr forming from its decay. Elucidation of the influence of bromamine dose on HAA formation was beyond the scope of this work. However, these data do indicate that bromamines are significantly more reactive than chloramines; and therefore may be important contributors to HAA formation in waters that contain bromide.

6.4. BROMOCHLORAMINE REACTIVITY

Lake Austin source water was dosed with preformed bromochloramine stock solutions at pH 6.3 and 7.2. Because bromochloramine formation is very dependent on pH (Trofe *et al*., 1980), solutions at pH 9 did not promote significant bromochloramine formation. Experiments were performed at pH 7.2 to to provide consistency with the bromamine reactivity experiments. Again, like the bromamine reactivity experiments, carbonate or phosphate buffers were used to maintain the desired pH, but only small concentrations were used to minimize any undesired reactions that may occur. A

summary of the bromochloramine reactivity experimental conditions is shown if Table 6-4.

Total combined oxidant and monochloramine concentrations were measured immediately after dosing and at various times thereafter. The bromochloramine concentration was approximated as the difference between these two measurements because MIMS analysis indicated that a majority of the bromine-substituted haloamine was bromochloramine. A more detailed analysis of the bromochloramine concentration is provided in Chapter 7. Greater concentrations of bromochloramine were observed in the dosing solution maintained at pH 6.3. However, the haloamine residual in this solution also decayed faster than the solution incubated at pH 7.2. For example, after 4 hours the water incubated at pH 6.3 only contained 0.5 mg Cl_2/L of total oxidant, while the water incubated at pH 7.2 contained 4.4 mg Cl_2/L. Therefore, incubation at pH 6.3 provided greater initial concentrations of bromochloramine, but at pH 7.2, the bromochloramine residual was maintained for a longer time.

Table 6-4 - Summary of bromochloramine reactivity experiments in Lake Austin source water

pH	**Carbonate Concentration (mM)**	**Phosphate Concentration (mM)**	**Initial Dose* (NH_2Cl; NHBrCl) (mg Cl_2/L)**	**Initial Dose* (NH_2Cl; NHBrCl) (mM)**
6.3	3.6	0	4.2; 2.9	0.058; 0.020
7.2	2.7	0.9	5.5; 1.8	0.078; 0.013

* NH_2Cl measured by Hach method 10171; NHBrCl determined by difference between the total oxidant concentration measured by Hach DPD method 8021 and the NH_2Cl concentration

The different bromochloramine doses resulted in significant HAA yields (Figure 6-5), indicating that bromochloramine is reactive enough to play a significant role in HAA formation. A majority of the HAA formed was DBAA; however, significant quantities of TBAA and MBAA were also measured. Only small amounts of BCAA formed; therefore, a majority of the HAA formed was bromine-substituted. Because the bromochloramine stock solutions formulated contained significant concentrations of monochloramine, controls were run with monochloramine to determine relative differences in reactivity. These experiments were conducted at the same pH, buffer concentration, and initial chloramine dose as the bromochloramine reactivity experiments. Results indicated that bromochloramine was more reactive than monochloramine (Figure 6-6). After 24 hours, significantly more HAA formed in the waters dosed with bromochloramine. In addition, since Lake Austin source water contains some bromide (168 μg/L), both bromine-and chlorine-substituted HAAs formed when the water was chloraminated. However, when the water was dosed with the bromochloramine solution, most of the HAAs were bromine-substituted. Therefore, the bromine-substituted halogen was significantly more reactive than the chlorine-substituted halogen also present, out-competing it for available reactive NOM sites.

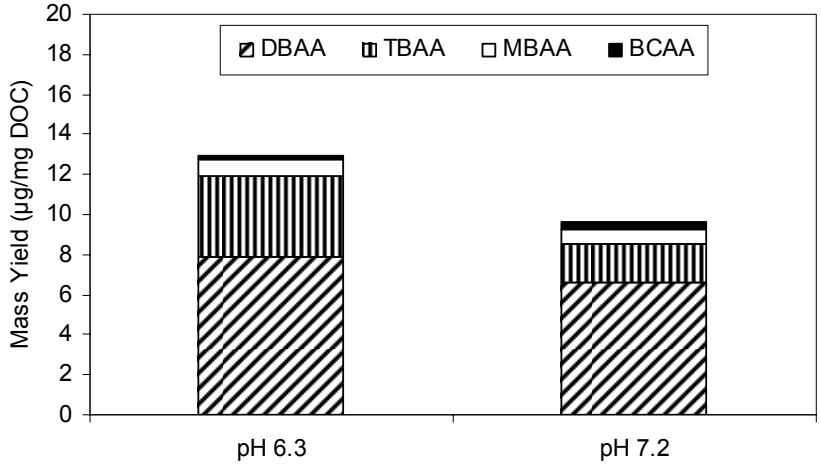


Figure 6-5 - HAA yield and speciation in Lake Austin source water after 24 hours incubation (Experimental Conditions: pH 6.3: 5:1 Br^-/NH_2Cl molar ratio, 3.6 mM total carbonate; pH 7.1: 5:1 Br^-/NH_2Cl molar ratio, 2.7 mM total carbonate, 0.9 mM total phosphate)

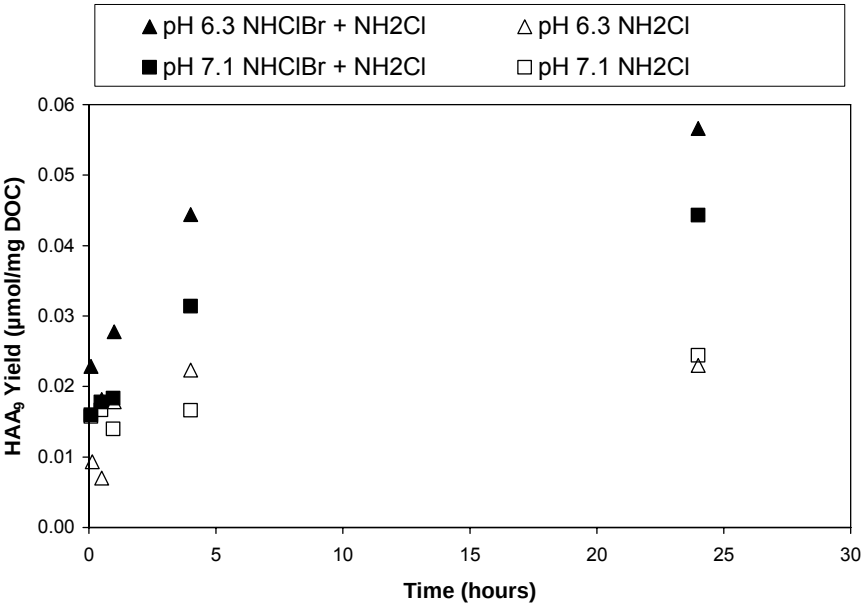


Figure 6-6 – Bromochloramine reactivity in Lake Austin source water (Experimental Conditions: pH 6.3 NHClBr + NH_2Cl: 5:1 Br^-/NH_2Cl molar ratio, 3.6 mM total carbonate; pH 7.1 NHClBr + NH_2Cl: 5:1 Br^-/NH_2Cl molar ratio, 2.7 mM total carbonate, 0.9 mM total phosphate; pH 6.3 NH_2Cl: Cl_2/N mass ratio = 4, NH_2Cl_o = .056 mM; pH 7.1 NH_2Cl: Cl_2/N mass ratio = 4, NH_2Cl_o = .077 mM)

Bromochloramine or one of its decomposition products is responsible for the observed HAA formation. NHBrCl can form from reactions of monochloramine with bromide or HOBr. Trofe *et al*. (1980) postulated the reaction mechanism:

$$NH_2Cl + H^+ \leftrightarrow NH_3Cl^+ \quad (4)$$

$$NH_3Cl^+ + Br^- \rightarrow NH_3Br^+ + Cl^- \quad (5)$$

$$NH_3Br^+ + NH_2Cl \rightarrow NHBrCl + NH_4^+ \quad (6)$$

The equilibrium constant for Equation 4 for is 28 M^{-1} (Gray *et al*., 1978). Therefore, under drinking water treatment conditions, only very small amounts of monochloramonium ion will be present. However, NH_3Cl^+ will react with bromide ion to form NH_3Br^+ (Equation 5) which rapidly reacts with monochloramine to form bromochloramine (Equation 6). This reaction mechanism demonstrates that NHBrCl formation increases as pH decreases. In addition, Gazda and Margerum *et al.* (1994) showed that monochloramine reacts with HOBr to form NHBrCl. Once formed, NHBrCl decomposes. As reported by Gazda and Margerum (1994), Valentine (1983) proposed that NHBrCl decomposes in base to regenerate OBr^- as a final product by equation 7:

$$2NHBrCl + OH^- \rightarrow N_2 + 3H^+ + 2\ Cl^- + Br^- + OBr^- \quad (7)$$

Therefore, in addition to NHBrCl, its decomposition products, such as HOBr, may be responsible for the HAAs formed in the presence of NOM.

6.5. SUMMARY

The bromine-substituted haloamines monobromamine, dibromamine, and bromochloramine are significantly more reactive than monochloramine in forming HAAs. Therefore, even though they are present in much lower concentrations than monochloramine under drinking water treatment conditions, they are still reactive enough to play a role in HAA formation. Metedeconk River source water was more reactive than Lake Austin, forming greater HAA yields in the presence of monobromamine,

dibromamine, and monochloramine (Figure 6-7). These data illustrate the importance of source water characteristics on the relative reactivity of each species. The greater reactivity of Metedeconk River was expected based upon its higher SUVA (4.87) compared to Lake Austin (2.11). Therefore, the varying characteristics of NOM among source waters is a significant factor in determining NOM's reactivity with the different bromine- and chlorine-substituted haloamines that may form in the presence of bromide during chloramination.

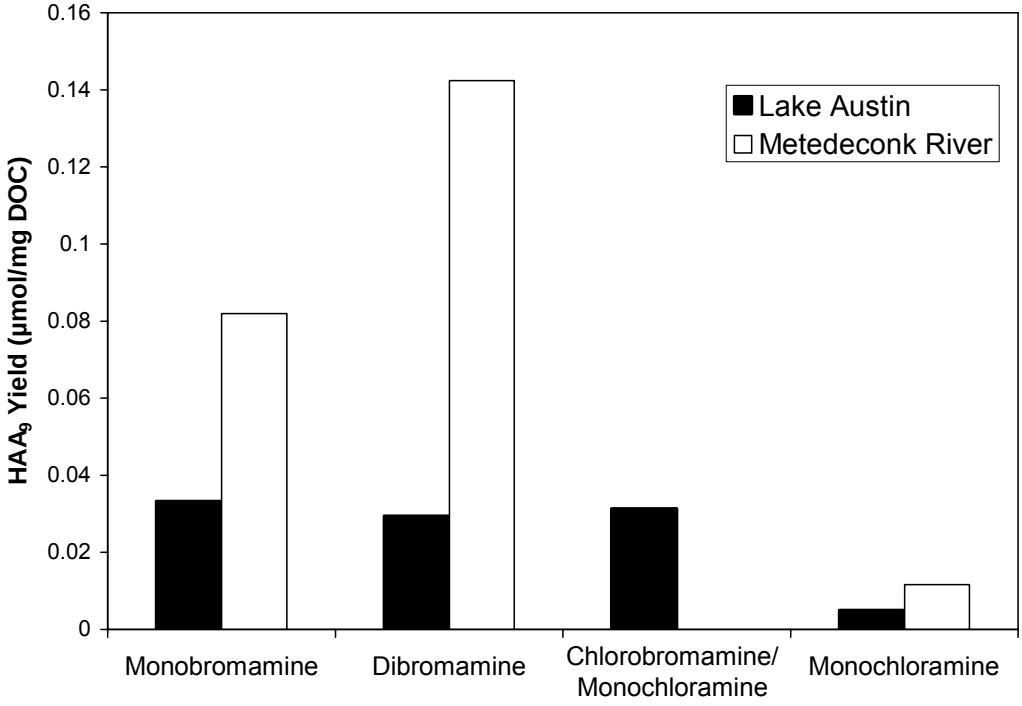


Figure 6-7 – Different haloamine reactivities in Lake Austin and Metedeconk River source waters after 4 hour incubation at pH 7.2 (All solutions were dosed to achieve between 0.5 and 1 mg Cl_2/L at 24 hours, except monochloramine, which was dosed to achieve a 2 mg Cl_2/L at 24 hours)

CHAPTER 7: Haloamine Speciation, Decay, and Modeling

7.1. INTRODUCTION

The variability of DXAA formation and speciation in waters that contain bromide not only depends on the reactivity with NOM of the different haloamines that may be present, but also their concentrations. A better understanding of haloamine speciation in the presence of bromide under the range of conditions encountered in drinking water treatment, coupled with the reactivity of the various species in forming DXAA will allow approaches for minimizing DXAA formation to be developed.

7.2. BROMAMINE DECAY KINETICS

Natural waters from Lake Austin and Metedeconk River were dosed with preformed bromamine stock solutions. The pH and Br^-/N ratio of these solutions were selected to provide dosing solutions containing predominantly mono- or dibromamine. The data presented in the following section represent the bromamine decay observed in the bromamine reactivity experiments presented in Chapter 6.

Bromamines are significantly more reactive than the chloramines in forming HAAs, and decay much more rapidly. In Lake Austin source water (Figure 7-1), the bromamines decayed significantly more rapidly than the chloramines at both pH 7.2 and 9. In addition, the bromamine solution at pH 9 was predominantly monobromamine, and that at pH 7.2, predominantly dibromamine. Therefore, these data indicate that dibromamine decays more rapidly than monobromamine. Similar results were obtained in Metedeconk River source water. Dibromamine (Figure 7-2) decayed more rapidly than monobromamine (Figure 7-3), and each bromamine species decayed significantly more rapidly than monochloramine.

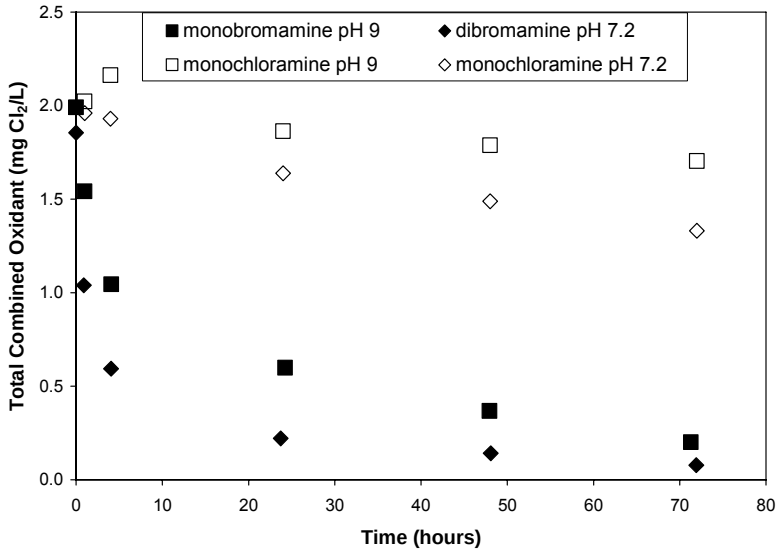


Figure 7-1 – Haloamine decay in Lake Austin source water (Experimental conditions: Monobromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.022 mM, $NHBr_{2o}$ = 0.003 mM; Dibromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.013 mM; Monochloramine pH 9: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM; Monochloramine pH 7.2: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM)

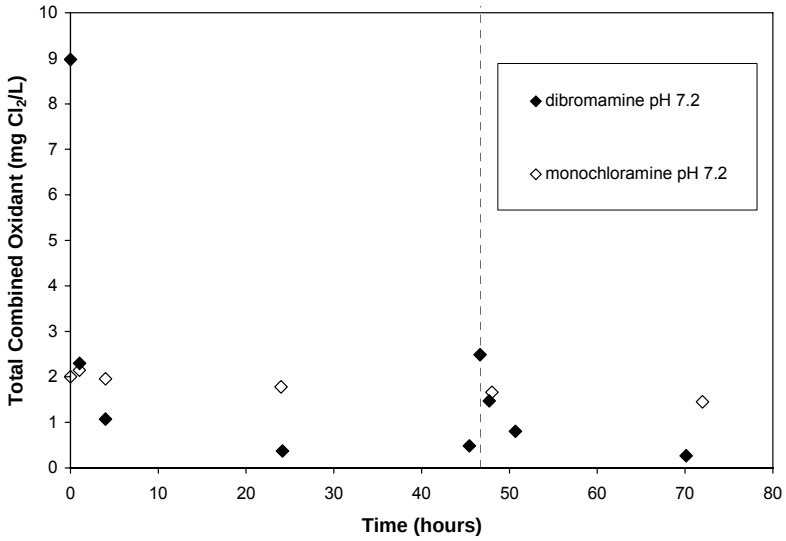


Figure 7-2 - Haloamine decay in Metedeconk River source water (Experimental conditions: Dibromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.063 mM; Monchloramine pH 7.2: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM; dashed line indicates time of additional bromamine spike)

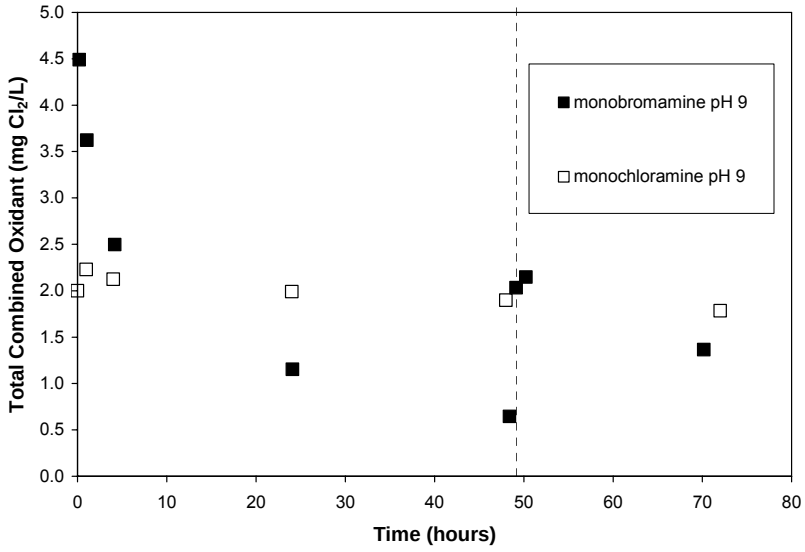


Figure 7-3 – Haloamine decay in Metedeconk River source water (Experimental conditions:Monobromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.056 mM, $NHBr_{2o}$ = 0.007 mM; Monochloramine pH 9: Cl_2/N mass ratio = 4, NH_2Cl_o = .0275 mM; dashed line indicates time of additional bromamine spike)

Natural organic matter can also influence haloamine decay. Figure 7-4 compares the monobromamine decay kinetics in both source waters with that in ultra pure water. Each of these waters was dosed with approximately 2 mg/L as Cl_2 of monobromamine, which decayed more rapidly in Metedeconk River source water than in Lake Austin source water. The greater reactivity of the NOM in Metedeconk River was not unexpected since it had a greater SUVA than Lake Austin (4.87 vs. 2.11) and a similar DOC concentration (3.01 vs. 3.45). In addition, it was also more reactive than Lake Austin in forming HAAs when dosed with chloramines or bromamines.

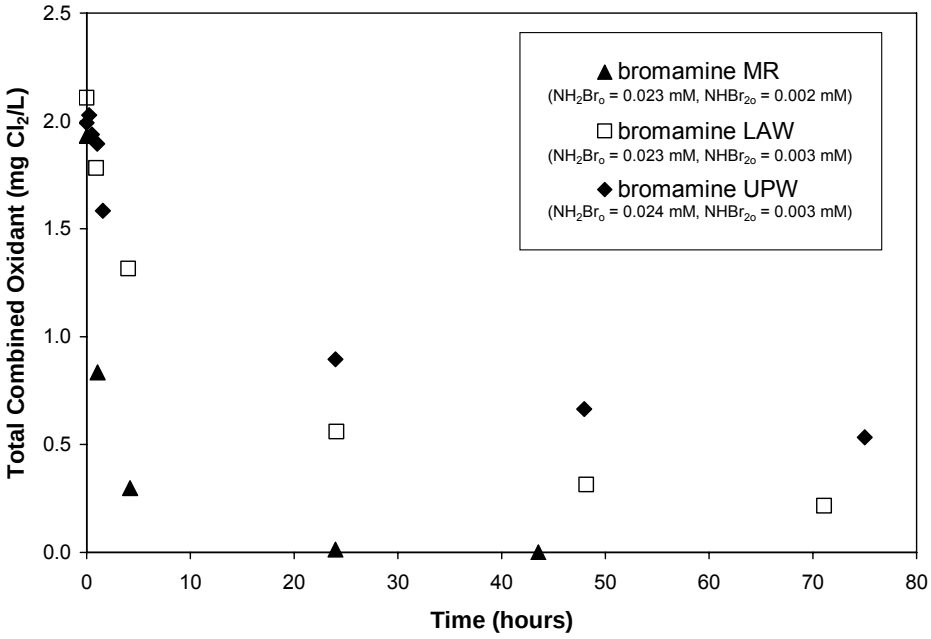


Figure 7-4 – Monobromamine decay kinetics in ultra pure water (UPW), Metedeconk River (MR), and Lake Austin (LAW) source waters (Experimental Conditions: pH 9 and Br_2/N molar ratio = 0.05; initial bromamine doses in parenthesis)

The influence of DOC on dibromamine decay was also investigated in Lake Austin and Metedeconk River source water. Both monobromamine and dibromamine decayed more rapidly in Lake Austin source water than in ultra pure water (Figure 7-5). These results were expected because bromamines were shown to be siginificantly more reactive than chloramines in forming HAAs. Similarly, monobromamine decayed more rapidly in Metedeconk River source water than in ultra pure water (Figure 7-6). However, in both Metedeconk River and ultra pure water the rate of dibromamine decay was essentially the same. Metedeconk River was dosed with a much higher dose of dibromamine than Lake Austin, and the kinetics of bromamine decay are more rapid at higher concentrations. Therefore, these decay reactions dominated over the bromamine - NOM reactions to such an extent that the influence of NOM could not be distinguished.

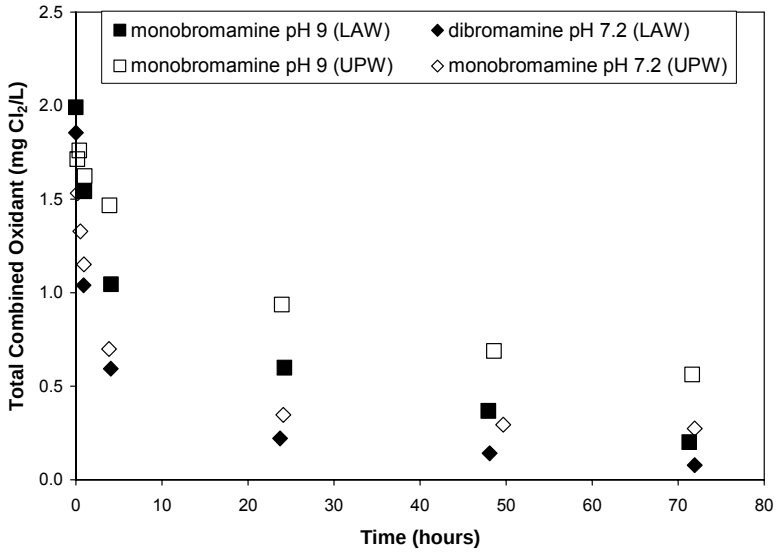


Figure 7-5 – Influence of DOC on bromamine decay in Lake Austin source water(LAW = Lake Austin source water; UPW = Ultra Pure Water; Experimental conditions: Monobromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.022 mM, $NHBr_{2o}$ = 0.003 mM; Dibromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.013 mM)

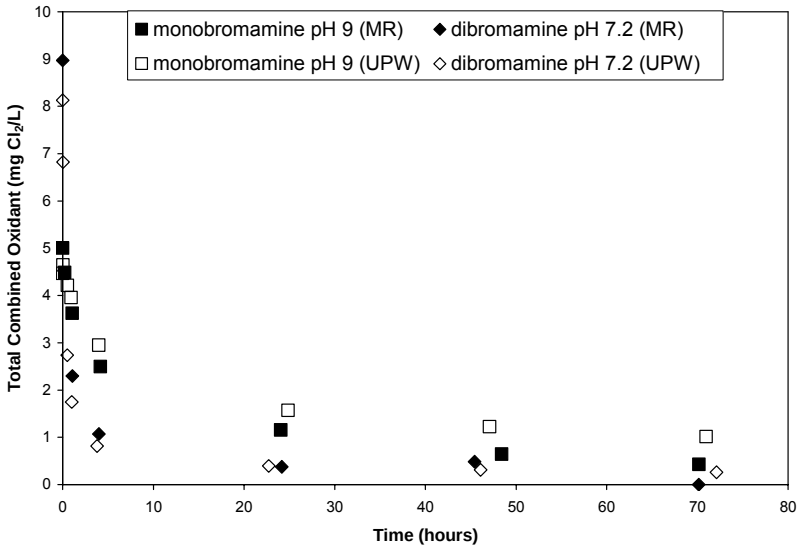


Figure 7-6 – Influence of DOC on bromamine decay in Metedeconk River source water (MR = Metedeconk River source water; UPW = Ultra Pure Water; Experimental conditions: Monobromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.056 mM, $NHBr_{2o}$ = 0.007 mM; Dibromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.057 mM)

Previous study of bromamine formation and decay showed that monobromamine predominates at high pH and low Br_2/N molar ratios, dibromamine predominates at lower pH and high Br_2/N molar ratios (Galal-Gorchev and Morris 1965), and that bromamines decay significantly faster than chloramines (Wajon and Morris 1980). Lei *et al*. (2004) studied bromamine decomposition kinetics in distilled water extensively in the pH range 6.5-9.5, at bromamine concentrations between 0.15-0.50 mM, and Br_2/N molar ratios between 0.01 and 0.2 Previous studies were conducted in the absence of NOM, typically at larger initial bromamine concentrations than those of this research, and were only monitored for minutes to hours, whereas in this research, bromamine decay was monitored for several days to simulate the detention time in distribution systems. This work showed that the trends of bromamine speciation and decay over longer time periods were similar to those previously observed.

7.3. BROMOCHLORAMINE DECAY KINETICS

Lake Austin source and ultra pure water was dosed with preformed bromochloramine stock solutions at pH 6.3 and 7.2 formed by reacting NH_2Cl and Br^- at a 5/1 Br^-/NH_2Cl mass ratio. Total combined oxidant and monochloramine concentrations were measured immediately after dosing and at various times thereafter. In addition, the haloamine decay was continuously monitored by MIMS. These measurements allowed the quantification of bromochloramine (Chapter 3 Section 3.14.5). In ultra pure water, this analysis indicated that these solutions contained predominantly monochloramine and bromochloramine, with only small amounts of dibromamine. The dibromamine concentration was typically less than 10% of the bromochloramine concentration; therefore, the bromochloramine concentration could be reasonably approximated as the difference between the total combined oxidant and monochloramine concentrations measured by Hach Methods 8021 and 10171, respectively.

Higher concentrations of bromochloramine were observed in ultra pure water at pH 6.3 (Figure 7-7) than at pH 7.2. However, the haloamine residual in this solution also decayed faster than the solution incubated at pH 7.2 (Figure 7-8). For example, after 4 hours the water incubated at pH 6.3 only contained 0.5 mg/L as Cl_2 of total oxidant, while the water incubated at pH 7.2 contained 4.4 mg/L as Cl_2. Therefore, incubation at pH 6.3 provided greater initial concentrations of bromochloramine, but at pH 7.2, the bromochloramine residual was maintained for a longer time. These two solutions illustrate the significant impact pH has upon bromochloramine formation and decay.

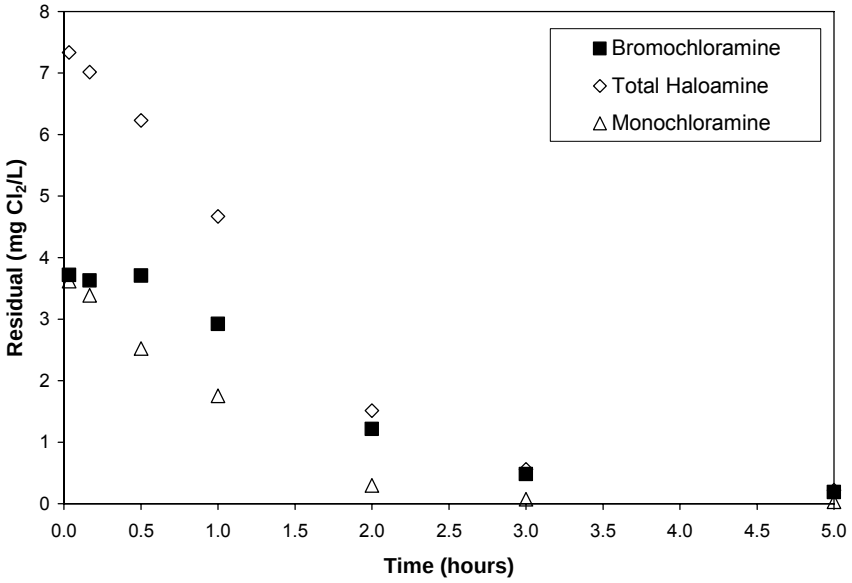


Figure 7-7 – Bromochloramine decay kinetics in Ultrapure Water (UPW) at pH 6.3 (5:1 Br^-/NH_2Cl molar ratio; 3.6 mM total carbonate)

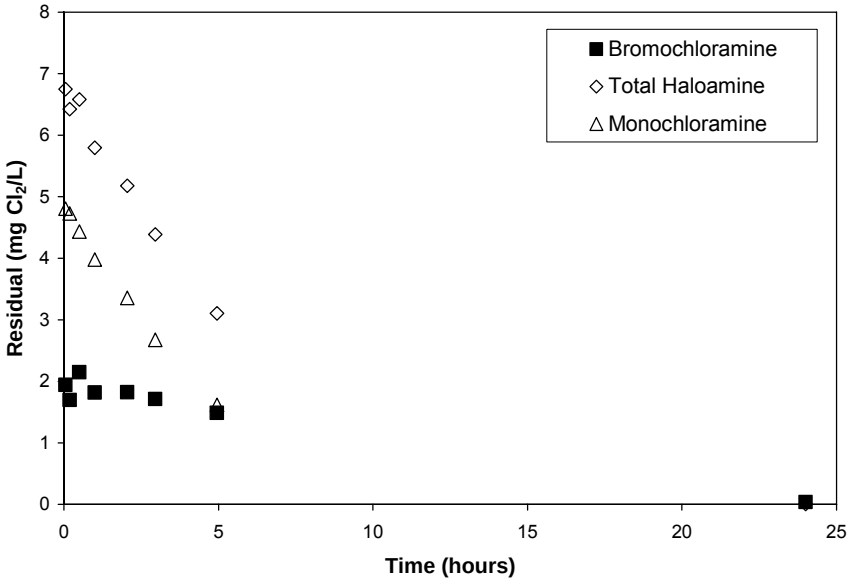


Figure 7-8 – Bromochloramine decay kinetics in Ultrapure Water (UPW) at pH 7.1 (5:1 Br^-/NH_2Cl molar ratio; 2.7 mM total carbonate; 0.9 mM total phosphate)

Lake Austin source water was also dosed with bromochloramine dosing solutions at pH 6.3 and 7.2. Whether determined by spectroscopic techniques (Figure 7-9) or by MIMS (Figure 7-10), bromochloramine decay was similar in Lake Austin and ultra pure water. In Figure 7-10, the response at m/z = 53 ($NH_2{}^{37}Cl^{\cdot+}$) represents monochloramine, m/z=131 ($NH^{79}Br^{37}Cl^{\cdot+}$ and $NH^{81}Br^{35}Cl^{\cdot+}$) represents bromochloramine, and m/z=177 ($NH^{81}Br^{81}Br^{\cdot+}$) represents dibromamine. The large response at m/z 53 indicates that significant concentrations of monochloramine were present, while the low response at m/z 177 indicates only small concentrations of dibromamine were present in each experiment. At early reaction times, less than 0.5 hours, the bromochloramine response (m/z=131) was slightly less in Lake Austin source water than in ultra pure water at both pH 6.3 and 7.1. Therefore, the bromochloramine may have reacted with some of the NOM present in Lake Austin source water. Once this demand was satisfied, after approximately 1 hour, the bromochloramine concentrations were similar in both waters.

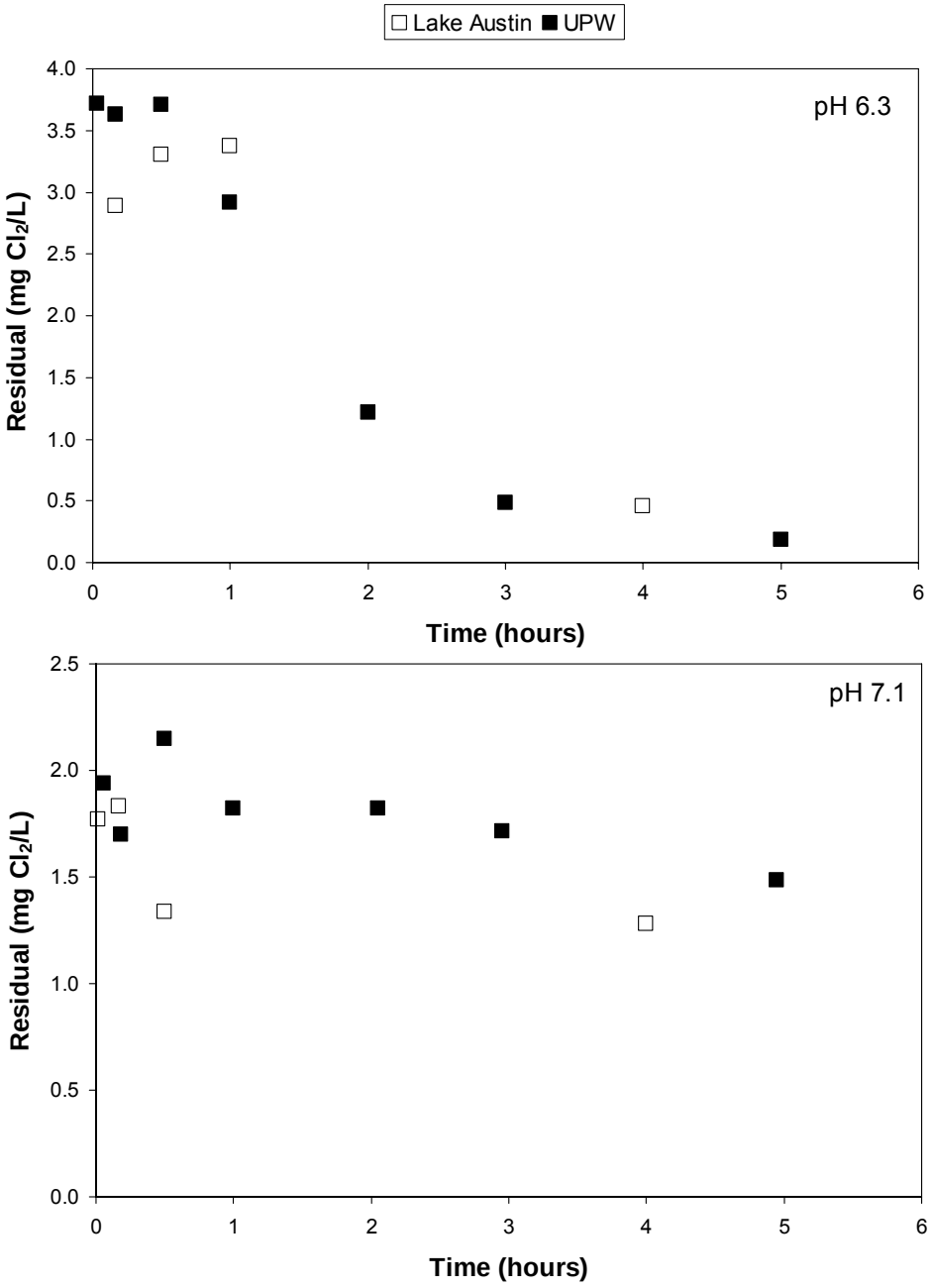


Figure 7-9 – Bromochloramine decay kinetics in Lake Austin source water and Ultra Pure Water (UPW) at pH 6.3 (5:1 Br^-/NH_2Cl molar ratio; 3.6 mM total carbonate) and pH 7.1 (5:1 Br^-/NH_2Cl molar ratio; 2.7 mM total carbonate; 0.9 mM total phosphate)

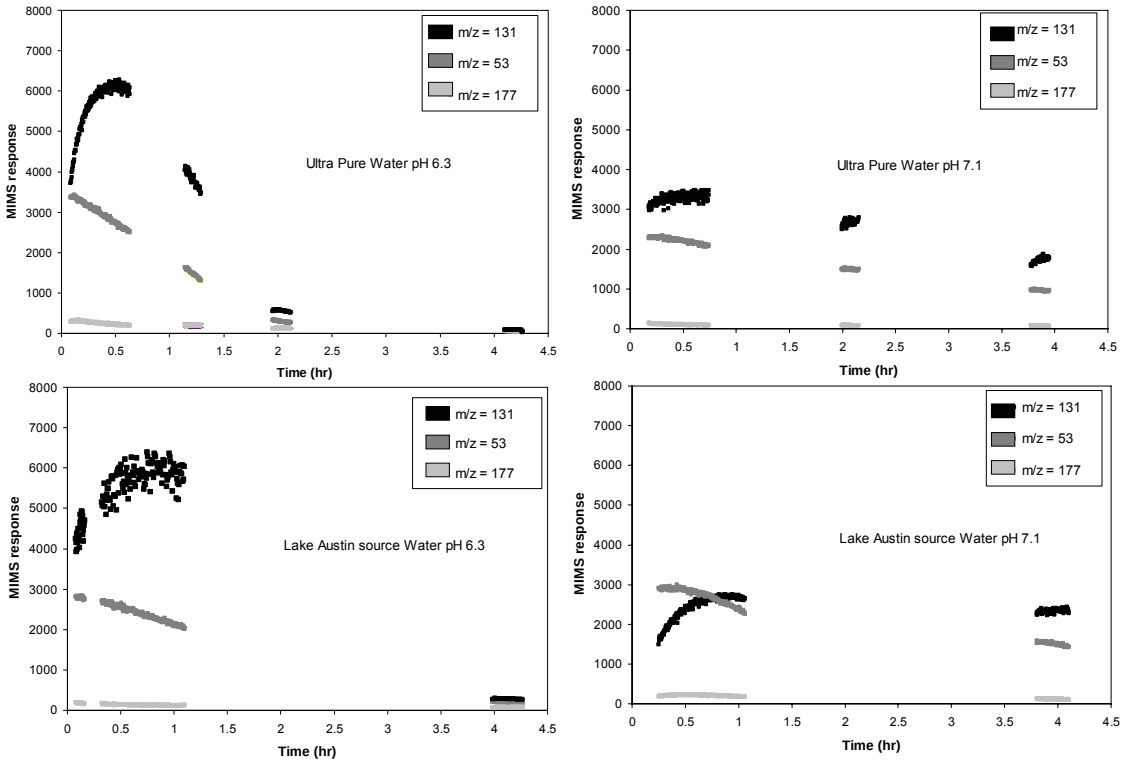


Figure 7-10 – MIMS analysis of haloamine decay (MIMS response at m/z = 53 ($NH_2{}^{37}Cl^{+}$) represents monochloramine, m/z=131 ($NH^{79}Br^{37}Cl^{+}$ and $NH^{81}Br^{35}Cl^{+}$) represents bromochloramine, and m/z=177 ($NH^{81}Br^{81}Br^{+}$) represents dibromamine) Each data point represents 15 second average of MIMS response

The minimal influence of NOM on NHBrCl decay indicates that this haloamine behaves more like dibromamine than monobromamine or monochloramine. The similarities observed between $NHBr_2$ and NHBrCl indicate that because dihaloamines decay rapidly, the presence of NOM has a small effect on their decay because decay is not dominated by NOM reactions, but rather by autodecomposition reactions. Experiments with $NHBr_2$ and NHBrCl (Figure 7-5, and Figure 7-8, respectively) at pH 7.2 indicate that NHBrCl decays more rapidly than $NHBr_2$ under the conditions studied in this research. The presence of NOM had a greater effect on NH_2Br decay than $NHBr_2$ decay in both Lake Austin and Metedeconk River source waters because NH_2Br decays

more slowly than $NHBr_2$ and NHBrCl, allowing haloamine-NOM reactions to contribute more to haloamine decay. The bromamine decay reactions are analogous to the chloramine system. Under drinking water treatment conditions, chloramine decomposition is limited by the rate of dichloramine formation, which then rapidly decomposes. Therefore, each of the dihaloamine species that may be present in drinking water ($NHCl_2$, $NHBr_2$, NHBrCl) behave similarly with respect to decay. In addition, because the bromine-substituted haloamines are significantly more reactive than chlorine-substituted haloamines, both $NHBr_2$ and NHBrCl may also behave similarly with respect to DBP formation.

7.4. UNIFIED HALOAMINE KINETIC MODEL

A unified haloamine kinetic model was developed to aid in understanding the complexity of haloamine chemistry. The model consists of a system of ordinary differential equations for the rate expressions and algebraic expressions for the equilibrium expressions that describe the reactive system. Experimental results were compared to model results obtained by solving the equations using the software package *Scientist* (1995), which uses Gear's Method to solve simultaneous differential equations. A literature search was conducted to determine the significance of reactions as well as their corresponding rate constants. If rate constants were not available in the literature, the model was used to estimate them using non-linear regression analysis techniques. *Scientist* (1995) uses a modified Powell algorithm to minimize the unweighted sum of the squares of the residual error between the predicted and experimentally observed values to estimate specific parameters in the model. Upper and lower bounds were placed on each parameter to be estimated so as not to exceed reasonable estimates.

The model consists of the monochloramine autodecomposition model developed by Jafvert and Valentine (1992) and Vikesland *et al*. (2001) (Table 7-1), as well as

reactions that incorporate bromide (Table 7-2). These reactions include the bromamine decomposition model developed by Lei *et al*. (2004) (Reactions 19-22), bromochloramine formation reactions (Trofe *et al.,* 1980 and Gazda and Margerum 1994) (Reactions 23 and 25), as well as various HOBr (Kumar and Margerum 1987) and NH_2Br (Wajon and Morris 1980) formation reactions.

In general, OBr^- has been shown to to be more reactive than OCl^-; and therefore, reactions with OBr^- have been included in the model. The rate of formation of monochloramine from free chlorine and ammonia occurs between the nonionic species, HOCl and NH_3. Qiang and Adams (2004) determined that the pathway between the ionic species, OCl^- and NH_4^+ to be mechanistically implausible. However, both HOBr and OBr^- can react with ammonia to form monobromamine (Wajon and Morris 1980). HOBr is about 1000 times more reactive toward NH_3 as OBr^- (Table 7-2). Therefore, the major pathway for monobromamine formation can be represented by the nonionic species (HOBr and NH_3) at pH <11 (Wajon and Morris 1980). However, the reaction with OBr^- is included in the model for completeness. Also, Gazda and Margerum (1994) determined that both OBr^- and HOBr react with NH_2Cl to form NHBrCl. The rate constants of each of these pathways (reaction 23 and 24 in Table 7-2) indicate both are important, and as such, are included in the model. In addition, both HOCl and OCl^- have been shown to react with Br^- to form HOBr (Kumar and Margerum 1987). However, the rate constant for the $OCl^- + Br^-$ reaction is only 9.0×10^{-4} $M^{-1}s^{-1}$, whereas the rate constant for $HOCl + Br^-$ is much greater at 1.55×10^3 $M^{-1}s^{-1}$. Therefore, the reaction with OCl^- was not included in the model.

Table 7-1 – Monochloramine autodecomposition model

No.	Reaction	Rate or Equil-ibrium Constant	Reference
1	$HOCl + NH_3 \rightarrow NH_2Cl + H_2O$	$4.2 \times 10^6\ M^{-1}s^{-1}$	Jafvert and Valentine (1992)
2	$NH_2Cl + H_2O \rightarrow NH_3 + HOCl$	$2.1 \times 10^{-5}\ s^{-1}$	Morris and Isaac (1981)
3	$NH_2Cl + HOCl \rightarrow NHCl_2 + H_2O$	$2.8 \times 10^2\ M^{-1}s^{-1}$	Margerum *et al*. (1978)
4	$NHCl_2 + H_2O \rightarrow HOCl + NH_2Cl$	$6.4 \times 10^{-7}\ s^{-1}$	Margerum *et al*. (1978)
5	$NH_2Cl + NH_2Cl \rightarrow NHCl_2 + NH_3$	pH dependent*	Vikesland *et al*. (2001)
6	$NHCl_2 + NH_3 \rightarrow NH_2Cl + NH_2Cl$	$6.1 \times 10^4\ M^{-2}s^{-1}$	Hand and Margerum (1983)
7	$NH_2Cl + NHCl_2 \rightarrow N_2 + 3H + 3Cl^-$	$1.5 \times 10^{-2}\ M^{-1}s^{-1}$	Leao (1981)
8	$NHCl_2 + H_2O \rightarrow NOH + 2HCl$	$1.1 \times 10^2\ M^{-1}s^{-1}$	Jafvert and Valentine (1987)
9	$NOH + NHCl_2 \rightarrow N_2 + HOCl + HCl$	$2.8 \times 10^4\ M^{-1}s^{-1}$	Leao (1981)
10	$NOH + NH_2Cl \rightarrow N_2 + H_2O + HCl$	$8.3 \times 10^3\ M^{-1}s^{-1}$	Leao (1981)
11	$HOCl \leftrightarrow H^+ + OCl^-$	$pK_a = 7.54$	Bodner and Pardue (1995)
12	$NH_4^+ \leftrightarrow NH_3 + H^+$	$pK_a = 9.24$	Bodner and Pardue (1995)
13	$H_2CO_3 \leftrightarrow HCO_3^- + H^+$	$pK_a = 6.35$	Bodner and Pardue (1995)
14	$HCO_3^- \leftrightarrow CO_3^{2-} + H^+$	$pK_a = 10.33$	Bodner and Pardue (1995)

*$k_5 = kH^+[H^+] + kH_2CO_3[H_2CO_3] + kHCO_3^-[HCO_3^-]$ where $kH_2CO_3 = 11\ M^{-2}s^{-1}$, $kHCO_3^- = 0.22\ M^{-2}h^{-1}$, $kH^+ = 6944\ M^{-2}s^{-1}$

NOH is the unidentified monochloramine auto-decomposition intermediate

Table 7-2 – Important bromide – monochloramine reactions in drinking water treatment

No.	Reaction	Rate or Equil-ibrium Constant	Reference
15	$HOCl + Br^- \rightarrow HOBr + Cl^-$	$1.55 \times 10^3\ M^{-1}s^{-1}$	Kumar and Margerum (1987)
16	$HOBr + NH_3 \rightarrow NH_2Br + H_2O$	$7.5 \times 10^7\ M^{-1}s^{-1}$	Wajon and Morris (1980)
17	$OBr^- + NH_3 \rightarrow NH_2Br + OH^-$	$7.6 \times 10^4\ M^{-1}s^{-1}$	Wajon and Morris (1980)
18	$NH_2Br + H_20 \rightarrow HOBr + NH_3$	$1.5 \times 10^{-3}\ s^{-1}$	Haag and Lietzke (1980)
19	$NH_2Br + NH_2Br \rightarrow NHBr_2 + NH_3$	pH dependent*	Lei *et al.* (2004)
20	$NHBr_2 + NH_3 \rightarrow NH_2Br + NH_2Br$	pH dependent^	Lei *et al.* (2004)
21	$NH_2Br + NHBr_2 \rightarrow N_2 + 3H^+ 3Br^-$	pH dependent+	Lei *et al.* (2004)
22	$NHBr_2 + NHBr_2 + H_2O \rightarrow N_2 + HOBr + 3H^+ + 3Br^-$	$8.9\ M^{-1}s^{-1}$	Lei *et al.* (2004)
23	$HOBr + NH_2Cl \rightarrow NHBrCl + H_2O$	$2.86 \times 10^5\ M^{-1}s^{-1}$	Gazda and Margerum (1994)
24	$OBr^- + NH_2Cl \rightarrow NHBrCl + OH^-$	$2.2 \times 10^4\ M^{-1}s^{-1}$	Gazda and Margerum (1994)
25	$NH_2Cl + NH_2Cl + Br^- \rightarrow NHBrCl + Cl^- + NH_3$	pH dependent#	Trofe *et al*. (1980); This work
26	$NHBrCl + NHBrCl + H_2O \rightarrow N_2 + HOBr + HBr + 2HCl$	$17\ M^{-1}s^{-1}$	Valentine 1983; This work
27	$HOBr \leftrightarrow OBr^- + H^+$	$pK_a = 8.8$	Haag and Hoigne (1983)

*$k_{19} = 0.5\ M^{-1}s^{-1} + 5 \times 10^8\ M^{-2}s^{-1}\ [H^+] + 290\ M^{-2}s^{-1}\ [NH_4^+] + 540\ M^{-2}s^{-1}\ [HCO_3^-]$

^$k_{20} = 1\ M^{-1}s^{-1} + 1 \times 10^9\ M^{-2}s^{-1}\ [H^+] + 190\ M^{-2}s^{-1}\ [NH_4^+] + 180\ M^{-2}s^{-1}\ [HCO_3^-]$

+$k_{21} = 6.2\ M^{-1}s^{-1} + 8.3 \times 10^4\ M^{-2}s^{-1}\ [OH^-] + 3.2 \times 10^3\ M^{-2}s^{-1}\ [CO_3^{2-}]$

#$k_{25} = 8.3 \times 10^5\ M^{-2}s^{-1}[NH_2Cl][Br^-][H^+]$

7.4.1. Monochloramine decay

The unified haloamine kinetic model was used to predict the decay of monochloramine in ultrapure water. In the absence of bromide these reactions are well understood; and therefore, the monochloramine decomposition model (Vikesland *et al*.,

2001) predicts monochloramine decay at different concentrations, pH, Cl/N ratios, and bromide concentrations well. After the incorporation of the bromide-monochloramine reactions (Table 7-2), monochloramine decay was still predicted very well. Model predictions corresponded very well with experimental measurements at both pH 7.5 and 9 with and without bromide (Figure 7-11).

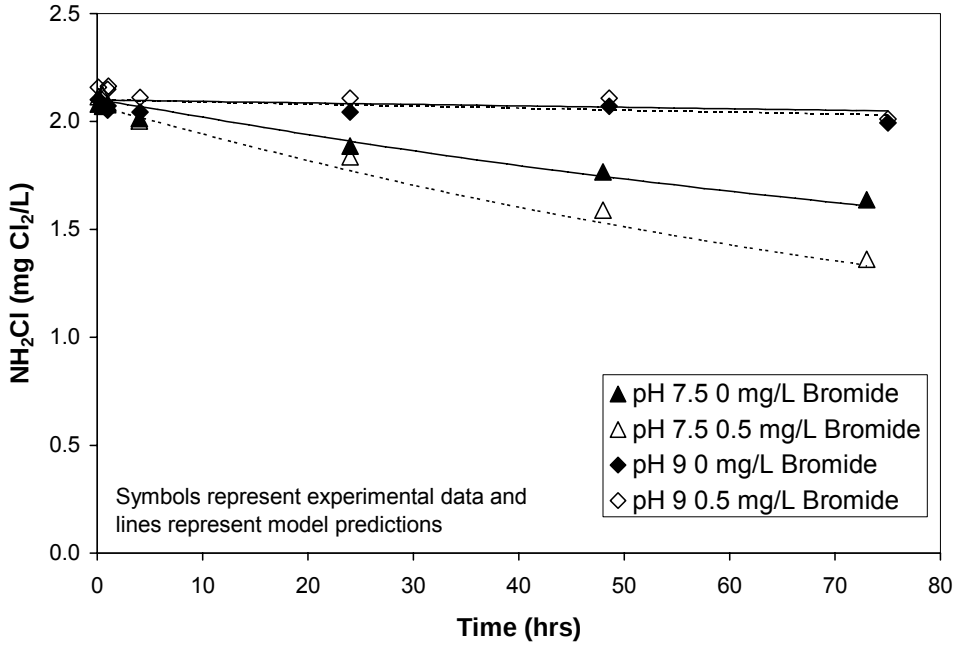


Figure 7-11 – Influnce of pH and bromide concentration on monochloramine decay in ultra pure water (Cl/N ratio molar ratio = 0.79)

7.4.2. Bromamine decay

The unified haloamine kinetic model was also used to predict the decay of bromamines in ultrapure water. In the absence of chlorine-substituted haloamines, the relevant equations in the unified model were the same as those proposed by Lei *et al.* (2004); therefore, good predictions of the experimental data were expected. Figure 7-12 and Figure 7-13 represent the bromamine decay controls run for the bromamamine

reactivity experiments with Lake Austin and Metedeconk River source waters, respectively.

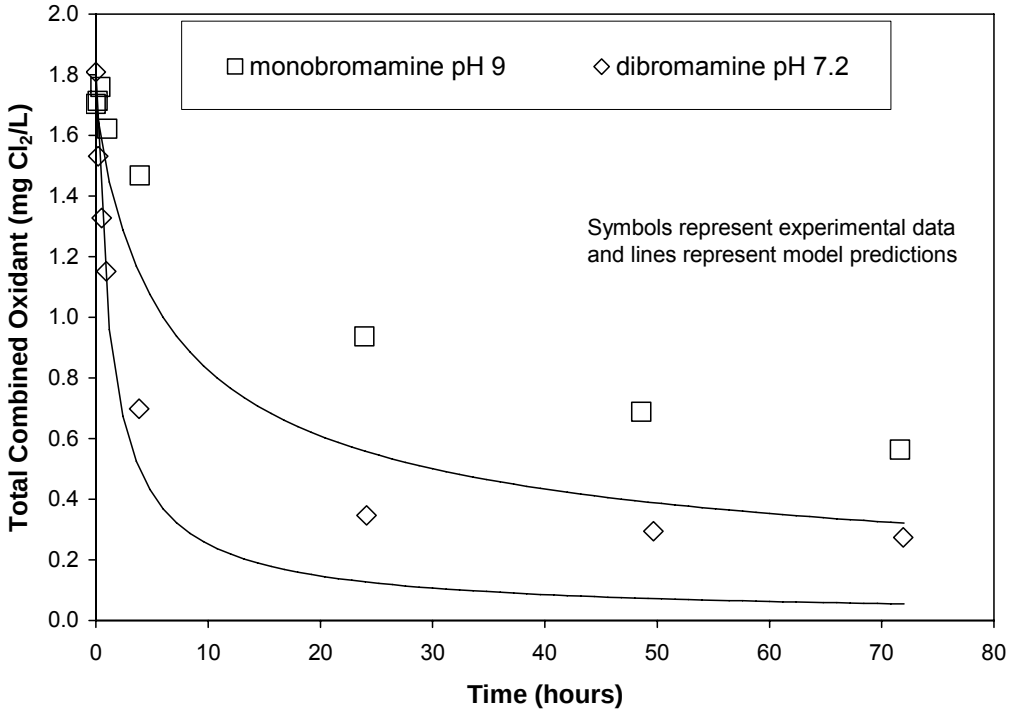


Figure 7-12 – Bromamine decay in ultra pure water (Experimental conditions: Bromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.022 mM, $NHBr_{2o}$ = 0.003 mM; Bromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.013 mM)

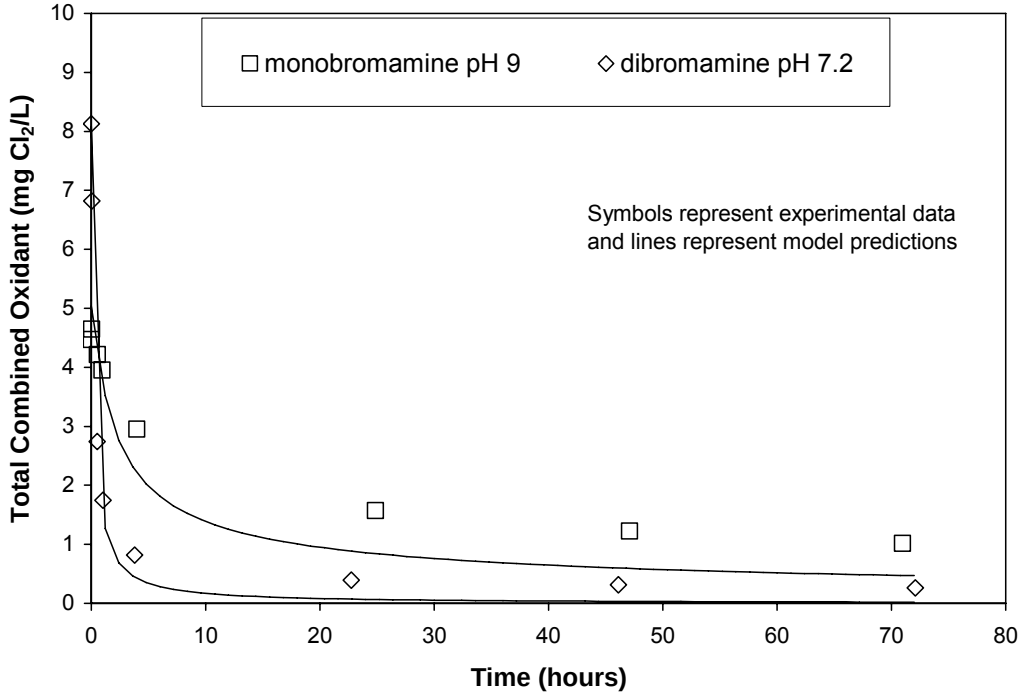


Figure 7-13 – Bromamine decay in ultra pure water (Experimental conditions: Bromamine pH 9: Br_2/N molar ratio = 0.05, NH_2Br_o = 0.056 mM, $NHBr_{2o}$ = 0.007 mM; Bromamine pH 7.2: Br_2/N molar ratio = 0.667, $NHBr_{2o}$ = 0.063 mM)

The experimental data and model predictions were in agreement at early reaction times; however, after the initial rapid decay during the first hour, the model somewhat underpredicted the bromamine residual in each experiment. Lei *et al*. (2004) used initial bromamine concentrations between 0.15 and 0.5 mM and only monitored the reactions for about 5 minutes, whereas these experiments had lower bromamine concentrations (less than 0.065 mM) and were monitored for 72 hours. In explaining the discrepancies between the predictions and measurement, it is first useful to note that the reactions for bromamine decomposition are analogous to those for chloramines. Hence, monobromamine disproportionates into dibromamine (reaction 19 in Table 7-2), and dibromamine hydrolysis (reaction 28) may result in an unidentified reaction intermediate

(I), which can react with $NHBr_2$ or NH_2Br (reactions 29 and 30) to form HOBr and various other products.

$$2NH_2Br \leftrightarrow NHBr_2 + NH_3 \quad (19)$$

$$NHBr_2 + H_2O \rightarrow I \quad (28)$$

$$I + NHBr_2 \rightarrow HOBr + products \quad (29)$$

$$I + NH_2Br \rightarrow products \quad (30)$$

Lei *et al.* (2004) simplified the reaction mechanism for the decay of dibromamine to reactions 21 and 22 in Table 7-2:

$$NHBr_2 + NHBr_2 \rightarrow products \quad (21)$$

$$NHBr_2 + NH_2Br \rightarrow products \quad (22)$$

The incorporation of the more robust reaction mechanism (reactions 19 and 28-30) into the unified model may result in better prediction of bromamine decay. However, rate constants were not available in the literature, and attempts to estimate them from data obtained in this study were unsuccessful. For example, good fits could be achieved at pH 7.2, but the new rate constants resulted in poorer fits at pH 9. Therefore, the rate constants and expressions determined by Lei *et al*. (2004) were used. Under conditions of drinking water treatment, the bromamine concentrations predicted by the model, as well as those measured by MIMS were typically significantly less than the concentration of the other key haloamines (monochloramine and bromochloramine); therefore, the simplified mechanism proposed by Lei *et al*. (2004) may be adequate. This discrepancy possibly will need to be addressed in the future if modeling efforts are extended to include haloamine reactions with NOM to predict DBP formation.

7.4.3. Bromochloramine decay

The formation and decay of bromochloramine was also simulated with the unified haloamine kinetic model. NHBrCl can form from reactions of monochloramine with bromide or HOBr. Trofe *et al*. (1980) postulated the reaction mechanism:

$$NH_2Cl + H^+ \leftrightarrow NH_3Cl^+ \quad (31)$$

$$NH_3Cl^+ + Br^- \rightarrow NH_3Br^+ + Cl^- \quad (32)$$

$$NH_3Br^+ + NH_2Cl \rightarrow NHBrCl + NH_4^+ \quad (33)$$

The combination of reactions 31-33 results in reaction 25 in Table 7-2. In addition, Gazda and Margerum *et al.* (1994) showed that monochloramine reacts with HOBr and OBr^- to form NHBrCl (Reactions 23 and 24 in Table 7-2).

Once formed, NHBrCl decomposes, although the best way to describe its decomposition reactions is still open to question. Valentine (1983) proposed that NHBrCl decomposes in base to regenerate OBr^- as a final product by reaction 34:

$$2NHBrCl + OH^- \rightarrow N_2 + 3H^+ + 2\ Cl^- + Br^- + OBr^- \quad (34)$$

The OBr^- formed from this reaction will react with NH_2Cl to reform NHBrCl (reaction 24 in Table 7-2); therefore, the net reaction of reactions 24 and 34 results in reaction 35:

$$NHBrCl + NH_2Cl \rightarrow N_2 + 3H^+ + 2\ Cl^- + Br^- \quad (35)$$

Vikesland *et al*. (2001) proposed that bromide would catalyze monochloramine decay according to the net reaction 36, which is the combination of reaction 25 in Table 7-2 with reaction 35.

$$3NH_2Cl + Br^- \rightarrow N_2 + NH_3 + 3H^+ + 3\ Cl^- + Br^- \quad (36)$$

Trofe proposed the rate expression for monochloramine loss in the presence of bromide to be:

$$r_{NH_2Cl} = -2k[NH_2Cl][Br^-][H^+] \quad (37)$$

which accurately predicts monochoramine loss, but not bromochloramine formation because it does not take into account the HOBr, formed as a result of bromochloramine decay, reacting with excess ammonia to reform NHBrCl. To accurately account for all reactive species in drinking water treatment, both the reaction mechanism proposed by Trofe *et al*. (1980) (reaction 25) as well as bromochloramine decay (reaction 26), as discussed below, were incorporated into the unified haloamine kinetic model. To account for the reformation of bromochloramine, new rate constants (k_{25} and k_{26} in Table 7-2) were estimated from the experimental data for bromochloramine formation and decay.

The decay of bromochloramine is likely to be analogous to that proposed for dichloramine and dibromamine. Therefore, bromochloramine hydrolysis (reaction 38) may result in an unidentified reaction intermediate (U), which can react with NHBrCl or NH_2Cl (reactions 39 and 40) to form HOBr and various other products.

$$NHBrCl + H_2O \rightarrow U \qquad (38)$$

$$U + NHBrCl \rightarrow HOBr + products \qquad (39)$$

$$U + NH_2Cl \rightarrow products \qquad (40)$$

This reaction mechanism, in which bromochloramine decay increases as pH increases, was incorporated into the model, but poor model fits of monochloramine decay and bromochloramine formation were obtained. The best model fits of both monochloramine and bromochloramine concentrations were obtained by using a simplified mechanism (reactions 25 and 26 of Table 7-2). This mechanism models bromochloramine decay in a manner similar to the approach of by Lei *et al.* (2004) for dibromamine decay. Therefore, the rate expression for bromochloramine decay is:

$$r_{NHBrCl} = -2k[NHBrCl][NHBrCl] \qquad (41)$$

Only the rate constants for reactions 25 and 26 of Table 7-2 were estimated using experimental data; other researchers previously determined all other rate constants in the

model. The rate constants for reactions 25 and 26 were determined independently at pH 6.3 and 7.2, and the resulting values were different at each pH. Therefore, an iterative approach was used to determine values for each rate constant that best fit the experimental data at both pH values. This mechanism resulted in good model fits of monochloramine decay, but somewhat less accurate fits of bromochloramine concentrations, especially at low pH values (Figure 7-14 and Figure 7-15). Limited data were available for model calibration, and only pH 6.3 and 7.2 were studied in this research. Therefore, more work is warranted to better determine the mechanism of bromochloramine decay and the associated rate constants.

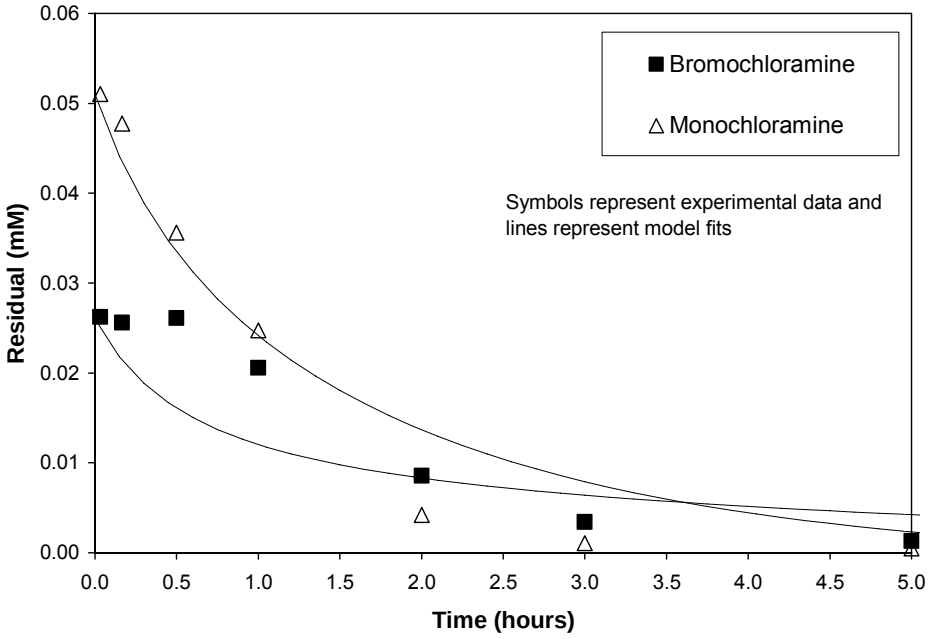


Figure 7-14 – Bromochloramine decay at pH 6.3

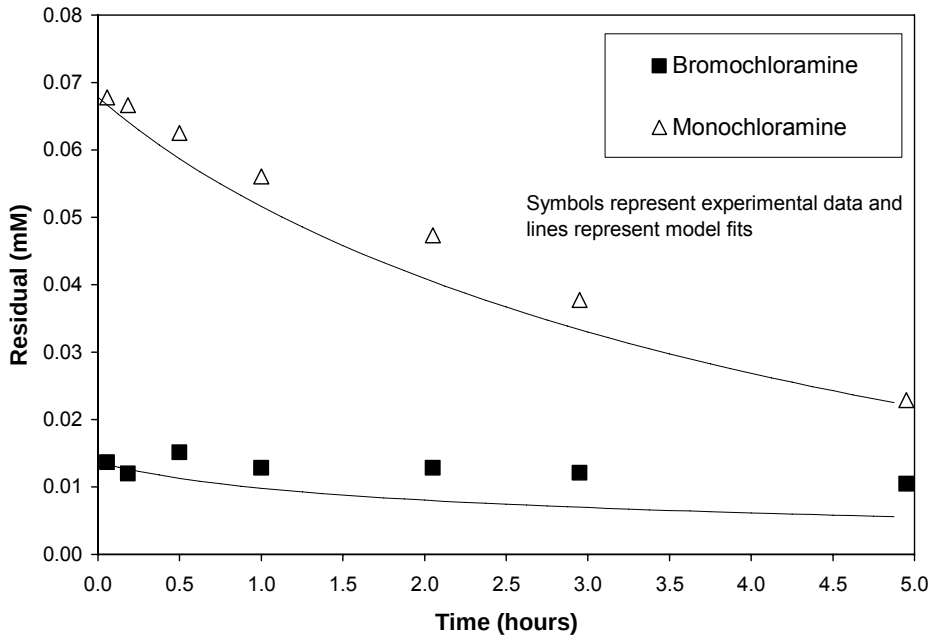


Figure 7-15 – Bromochloramine decay at pH 7.2

7.5. HALAOMINE SPECIATION EXPERIMENTS

Experiments were conducted in NOM-free, high-purity water to determine the influence of pH, bromide concentration, and prechlorination on haloamine speciation (Table 7-3). In each experiment, the ultra pure water was dosed with either 2 mg/L as Cl_2 preformed monochloramine or chlorine. In the prechlorination experiments, 0.5 mg/L as N ammonium sulfate was added after the 5-minute prechlorination period. Total combined oxidant and monochloramine concentrations were measured by spectroscopic techniques as well as by MIMS.

Table 7-3 – Summary of haloamine speciation experiments

Oxidant	pH	Bromide Concentration (mg/L)
Monochloramine*	9	0
Monochloramine*	9	0.5
Monochloramine*	7.2	0
Monochloramine*	7.2	0.5
5 min prechlorination**	9	0.5
5 min prechlorination**	7.2	0.5

* 4/1 Cl_2/N mass ratio; preformed chloramines

** 2 mg Cl_2/L HOCl followed by 0.5 mg N/L ammonia addition after 5 minutes

Water matrix – 3mM carbonate buffer in Ultra Pure Water (UPW)

7.5.1. Haloamine Formation and Decay during Chloramination

The results of the preformed chloramination experiments are summarized in Figure 7-16. Only monochloramine concentrations are shown because other chlorine- and bromine-substituted haloamines were not detected. At pH 9, the bromide concentration had a minimal influence on monochloramine decay, whereas at pH 7.2, the addition of bromide increased the decay rate of monochloramine. In addition, the model predictions corresponded well with the experimental results under the conditions studied.

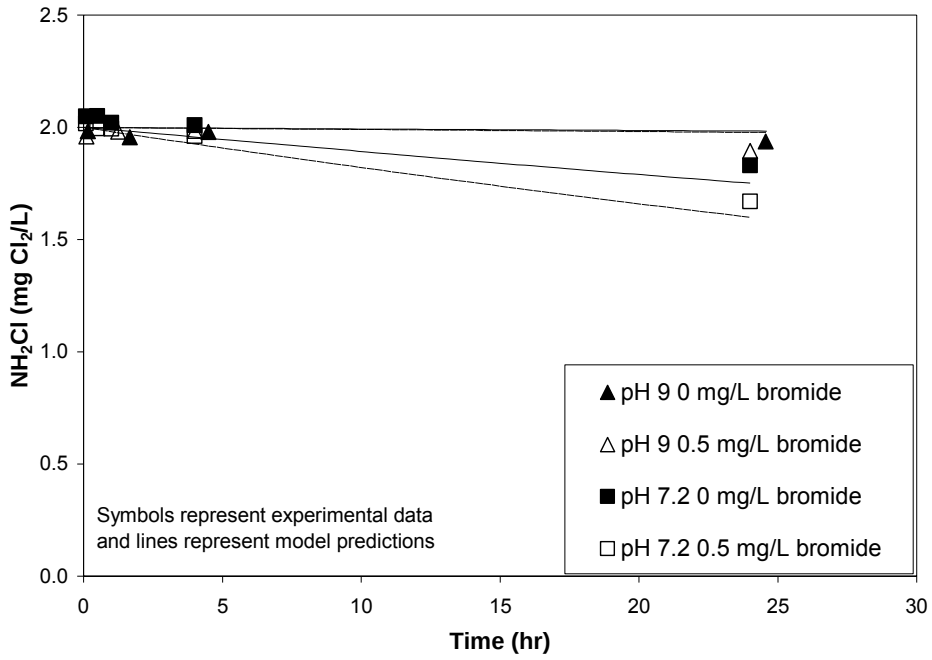


Figure 7-16 – Influence of pH and bromide concentration on monchloramine decay

7.5.2. Haloamine Formation and Decay after Prechlorination

Based on the results with chloramination, it was expected that pH should also impact haloamine speciation after prechlorination in the presence of bromide, especially at low pH. In the presence of bromide, prechlorination did not significantly impact monochloramine decay at pH 9 (Figure 7-17); however, at pH 7.2 (Figure 7-18), a significant effect was observed. Upon addition of ammonia after the 5-minute prechlorination period, 2 mg/L of total haloamine formed, of which only approximately 1.5 mg/L was monochloramine. However, after 24 hours, the monochloramine and total haloamine concentrations were essentially the same.

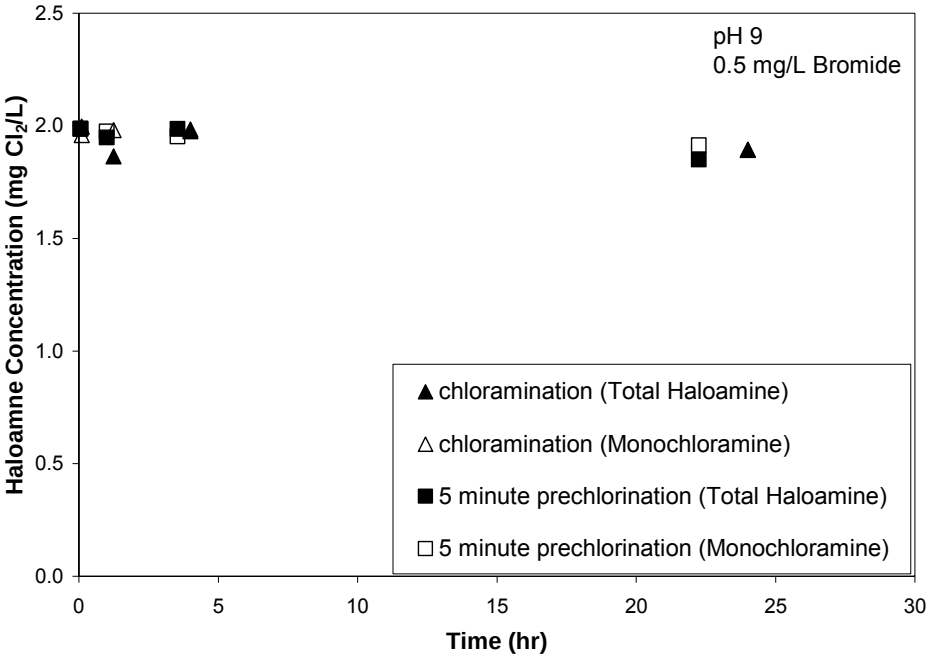


Figure 7-17 – Influence of prechlorination on haloamine speciation at pH 9

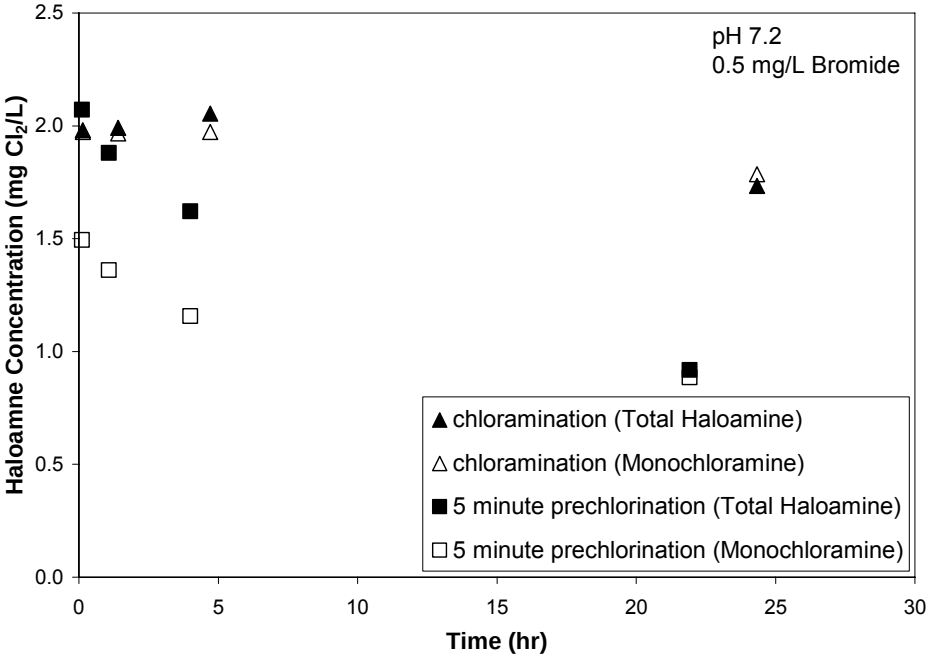


Figure 7-18 – Influence of prechlorination on haloamine speciation at pH 7.2

During prechlorination, the bromide can be oxidized by free chlorine to form HOBr (reactions 16 and 17 in Table 7-2). The pH effect observed in the prechlorination experiments results from the speciation of free chlorine and bromine between their more reactive (HOCl and HOBr) and less reactive forms (OCl^- and OBr^-). The pK_a of HOCl is 7.55; therefore, at pH 7.2 almost 70% of the total chlorine is in the more reactive form, whereas at pH 9 only about 3% is in this form. Higher concentrations of $HOBr/OBr^-$ were formed at pH 7.2 than at pH 9 because bromide oxidation by HOCl (rate constant = 1.55×10^3 $M^{-1}s^{-1}$) is over 100,000 times more rapid than by OCl^- (rate constant = 0.90×10^{-3} $M^{-1}s^{-1}$) (Kumar and Margerum 1987). When the prechlorination period is terminated by the addition of ammonia, monochloramine forms and the $HOBr/OBr^-$ present can react with it to form bromochloramine as well as with ammonia to form bromamines. HOBr is about 1000 times as reactive toward NH_3 as OBr^- (Table 7-2). Therefore, the major pathway for monobromamine formation can be represented by the nonionic species (HOBr and NH_3) at pH <11 (Wajon and Morris 1980). Also, Gazda and Margerum (1994) determined that both OBr^- and HOBr react with NH_2Cl to form NHBrCl, but HOBr is 10 times more reactive with NH_2Cl than OBr^- (reaction 23 and 24 in Table 7-2).

It was expected that the difference between the total haloamine concentration and monochloramine concentration was predominantly bromochloramine. MIMS was used to determine if bromochloramine was indeed the predominant bromine-substituted haloamine present. At pH 9 only monochloramine was detected by MIMS; however, at pH 7.2 significant concentrations of NHClBr and $NHBr_2$ were detected in addition to NH_2Cl (Figure 7-19). Besides simply monitoring specific ions, haloamine concentrations were determined by the methods outlined in Chapter 3 Section 3.14.5. Good agreement was achieved between the spectrometric techniques and MIMS at pH 9 (Figure 7-20) and 7.2 (Figure 7-21). In these figures, the sum of the NHBrCl and NH_2Br concentrations

determined by MIMS should be equivalent to the difference between the total haloamine and the monochloramine concentration determined by spectrometric techniques. Figure 7-22 illustrates the excellent agreement between the two independent analytical techniques. Although the MIMS measurements were slightly higher than the spectrometric measurements at all sampling times, this comparison nevertheless demonstrated that MIMS can accurately measure haloamine speciation.

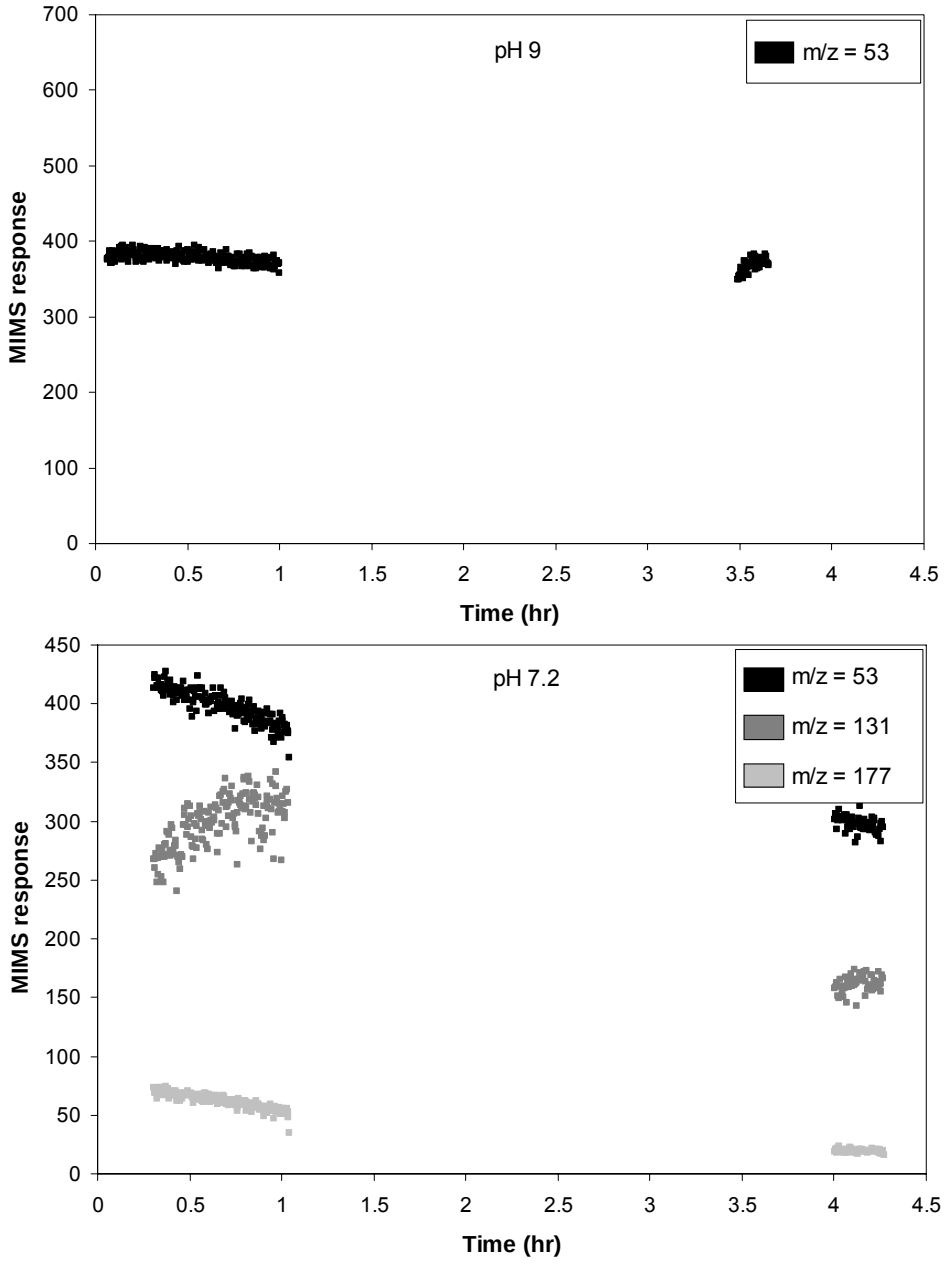


Figure 7-19 – Influence of pH on haloamine speciation in ultra pure water in the presence of 0.5 mg.L bromide after 5 minutes prechlorination (MIMS response at m/z = 53 ($NH_2{}^{37}Cl^{+}$) represents monochloramine, m/z=131 ($NH^{79}Br^{37}Cl^{+}$ and $NH^{81}Br^{35}Cl^{+}$) represents bromochloramine, and m/z=177 ($NH^{81}Br^{81}Br^{+}$) represents dibromamine) Each data point represents 15 second average of MIMS response

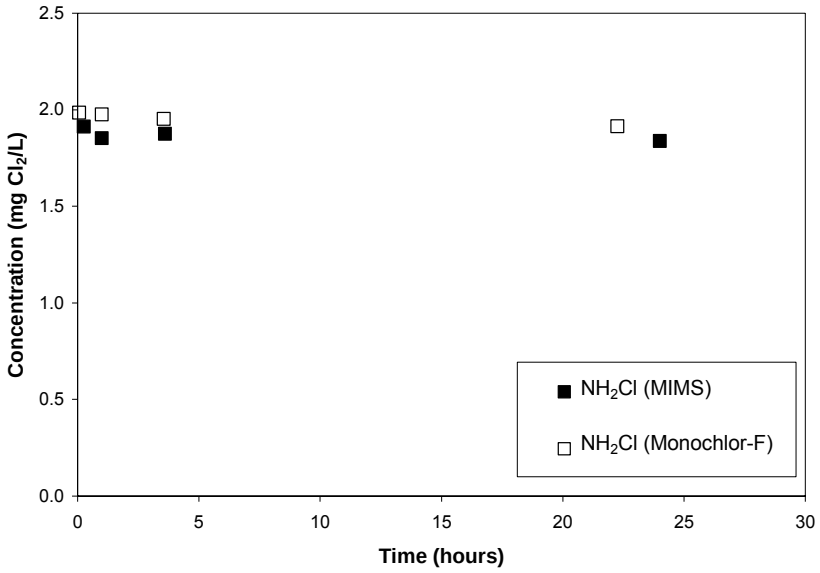


Figure 7-20 – Haloamine residual in ultra pure water – 5 minute prechlorination, 0.5 mg/L Br^-, and pH 9 (Solid symbols represent MIMS data and open symbols represent Hach method 10171)

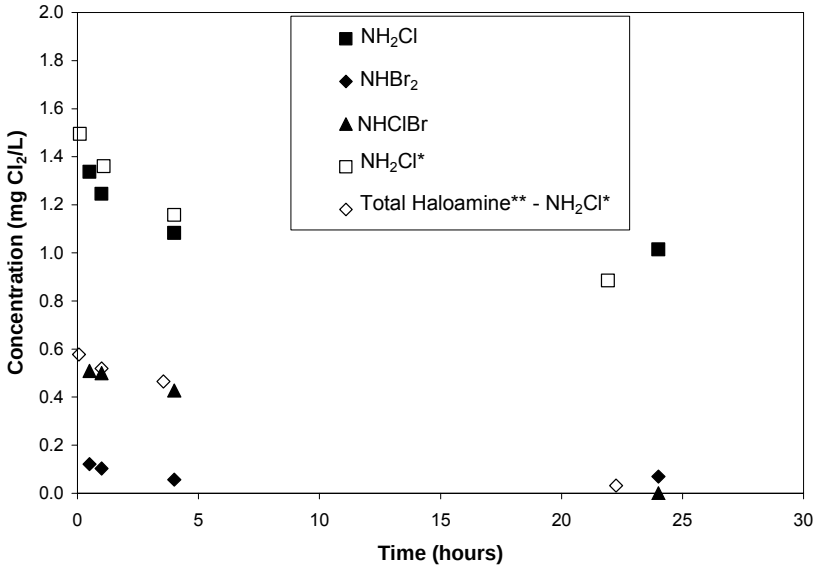


Figure 7-21 – Haloamine residual in ultra pure water – 5 minute prechlorination, 0.5 mg/L Br^-, and pH 7.2 (Solid symbols represent MIMS data and open symbols represent Hach methods: *Hach method 10171 and **Hach method 8167)

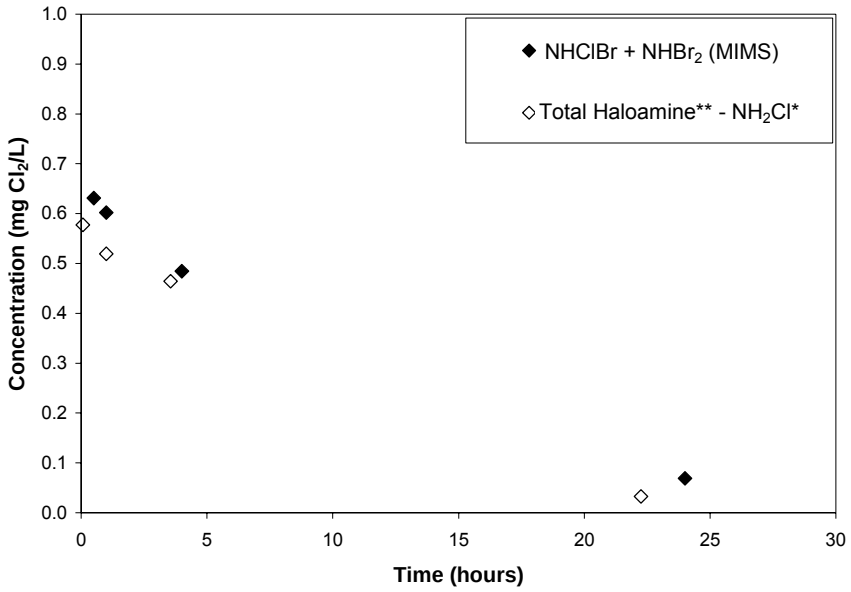


Figure 7-22 – Summation of NHBrCl and NH_2Br residual in ultra pure water – 5 minute prechlorination, 0.5 mg/L Br^-, and pH 7.2 (Solid symbols represent MIMS data and open symbols represent Hach methods: *Hach method 10171 and **Hach method 8167)

7.5.3. Modeling Haloamine Formation and Decay after Prechlorination

The pH has a significant influence on the formation of HOBr during prechlorination in the presence of bromide because the pK_a of HOCl is approximately 7.55, and HOCl is significantly more reactive than OCl^-, less HOBr will form at pH 9 than at pH 7.2. When ammonia is added to form monochloramine, the HOBr that is present will form NHBrCl and NH_2Br. Figure 7-23 and Figure 7-24 compare experimental data obtained by MIMS with predictions from the unified haloamine kinetic model, using rate constants from others and the bromochloramine decay experiments of this research (Table 7-1 and Table 7-2). The unified model accurately predicted that more HOBr formation occurred at lower pH, resulting in more NHBrCl formation when ammonia is added to form monochloramine. Excellent matches were obtained between the measured and predicted bromochloramine and dibromamine concentrations at both

pH 7.2 and 9. At the longer reaction times, the model tended to underpredict the NH_2Cl concentration and overpredict the NHBrCl concentration; this tendency is most obvious in the pH 7.2 results. The differences between the measured and predicted concentrations may be a result of discrepancies in the mechanism of bromochloramine decay, as previously discussed. Therefore, the elucidation of the mechanism of bromochloramine decay may result in better model predictions.

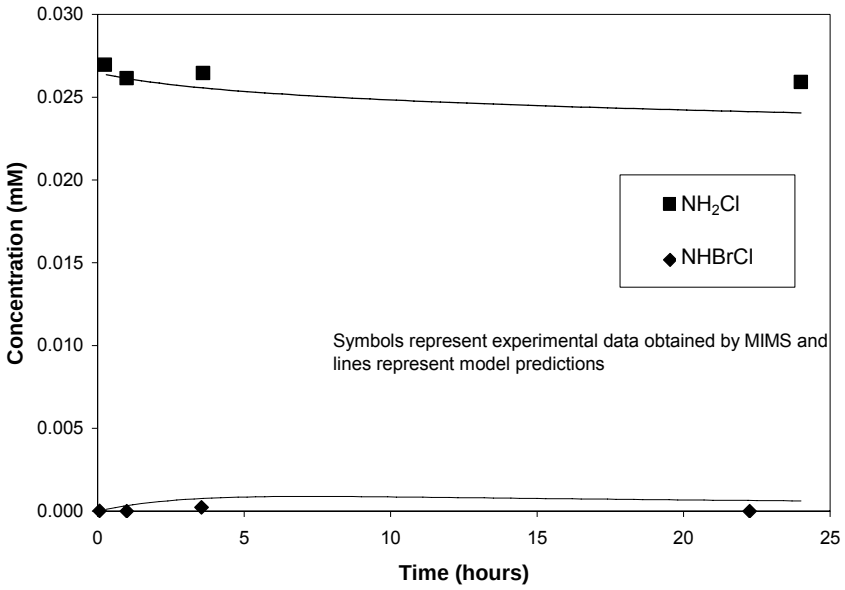


Figure 7-23 – Haloamine residual in ultra pure water – 5 minute prechlorination, 0.5 mg/L Br^-, and pH 9

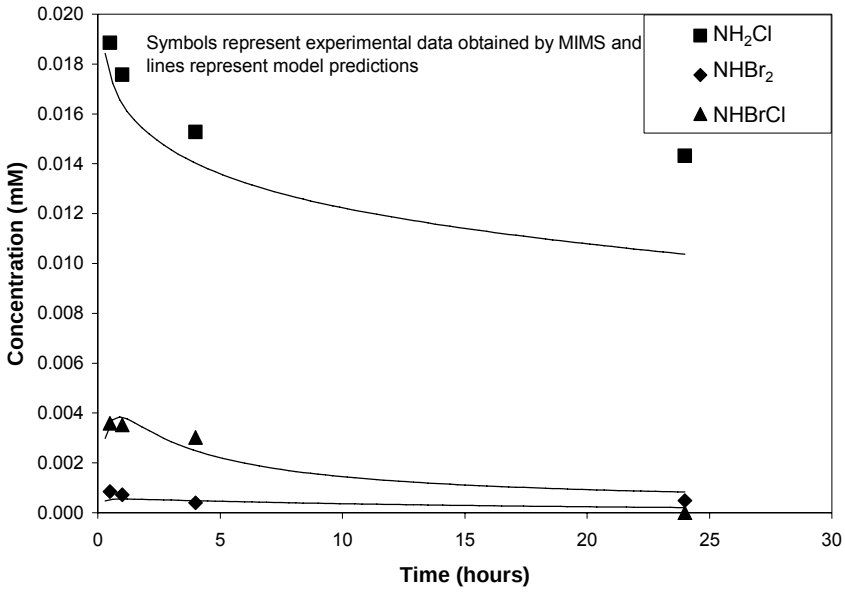


Figure 7-24 – Haloamine residual in ultra pure water – 5 minute prechlorination, 0.5 mg/L Br^-, and pH 7.2

In natural waters, the HOBr that forms as a result of prechlorination can react with NOM, forming DBPs. Significantly lower HOBr concentrations are expected to be present in natural water than in ultra pure water. Therefore, when the prechlorination is terminated by ammonia addition and monochloramine is formed, less HOBr will be available to form NHBrCl in natural waters than in ultra pure water. Further study of the influence of prechlorination on haloamine speciation in natural waters, coupled with the incorporation of oxidant-NOM reactions, is needed to accurately predict DBP formation.

7.5.4. Influence of the Method of Chloramine Addition on Haloamine Formation

In practice, chloramines are typically formed after a period of prechlorination or by the simultaneous (near simultaneous) addition of chlorine and ammonia. The simultaneous addition of chlorine and ammonia in waters that contain bromide may result in competition between NH_2Cl and HOBr formation. Once formed, the NH_2Cl and

HOBr will react to form NHBrCl. Therefore, the influence of simultaneous addition of chlorine and ammonia and preformed monochloramine on bromochloramine formation was investigated (Figure 7-25). In these experiments, Lake Austin source water spiked with different bromide concentrations was dosed with either preformed monochloramine or with ammonia followed by chlorine at a 4:1 Cl_2:N mass ratio in concentrations to form 2 mg/L monochloramine at pH 6.3. Higher concentrations of bromochloramine, monitored at m/z = 131 ($NH^{79}Br^{37}Cl^{+}$ and $NH^{81}Br^{35}Cl^{+}$), were observed in the waters where chlorine was added after ammonia than from preformed monochloramine. These results indicate that the manner of chloramine formation and addition can influence haloamine speciation, and therefore, DBP formation.

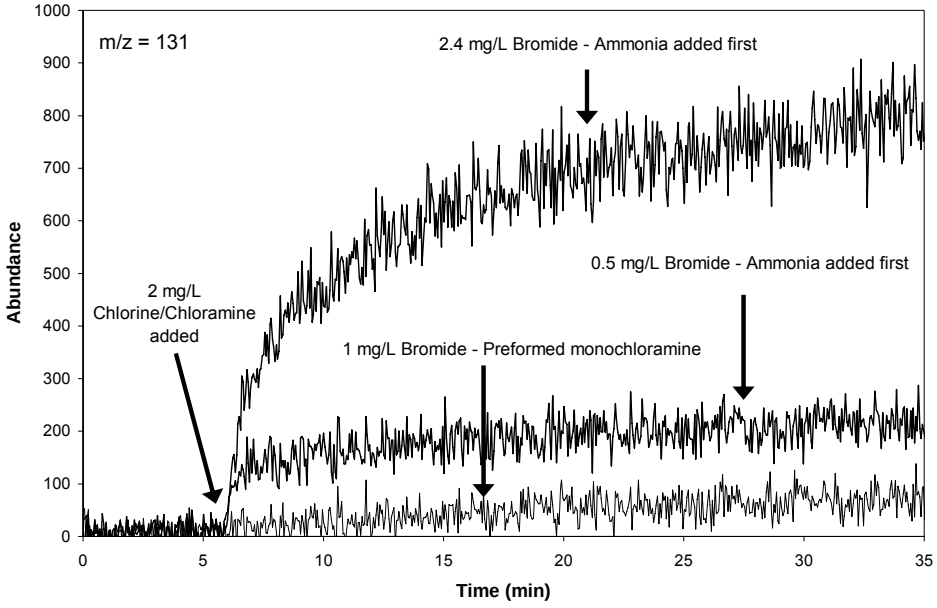


Figure 7-25 – Influence of order of chemical addition on bromochloramine formation pH 6.3 (m/z=131 represents $NH^{79}Br^{37}Cl^{+}$ and $NH^{81}Br^{35}Cl^{+}$)

The unified haloamine kinetic model was used to further investigate how the method of chloramine addition influences haloamine speciation. The impact of both

preformed chloramines and simultaneous addition of chlorine and ammonia in the presence of 150 μg/L bromide was predicted at pH 6 (Figure 7-26) and pH 9 (Figure 7-27). The pH not only has a large impact on monochloramine formation and decay, but also on the formation of bromine-substituted haloamines. Simultaneous chemical addition resulted in significantly less monchloramine formation and more dichloramine formation than preformed chloramines at pH 6. At pH 9, however, no impact was observed on monochloroamine or dichloramine (not shown) concentrations. At both pH 6 and 9, simultaneous chemical addition resulted in more bromine-substituted haloamine formation than with preformed chloramines. Because chloramine decay and bromochloramine formation are acid catalyzed, significantly greater bromine-substituted haloamine formation was predicted at pH 6 than at pH 9. At pH 6, NHBrCl was the predominant bromine-substituted haloamine present, whereas at pH 9, monobromamine predominated. The model was also used to investigate the effect of near-simultaneous chlorine and ammonia addition (10 second prechlorination). The brief period of prechlorination resulted in only slightly greater bromine-substituted haloamine formation at pH 6 (Figure 7-28) and 9 (Figure 7-29) than simultaneous chemical addition. These simulations illustrate the dramatic impact pH and the method of chemical addition has on haloamine speciation, and therefore, presumably DBP formation. The bromine-substituted haloamines are significantly more reactive than their chlorine-substituted counterparts in forming HAAs. Therefore, the increased concentration of these species at low pH likely results in greater bromine-substituted DBP formation, which correlates well with the studies of the influence of bromide and pH on HAA formation previously described (Section 4.4 and Section 5.3). DBP formation studies with brief periods of prechlorination are warranted to determine if utilities that treat high bromide source

waters would benefit from disinfecting with preformed chloramines made in low bromide water instead of simultaneous addition of chlorine and ammonia.

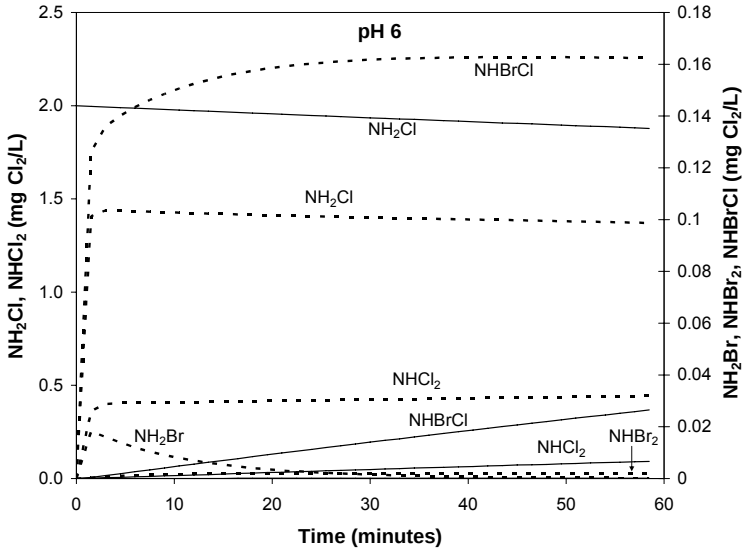


Figure 7-26 – Model predictions of haloamine formation from simultaneous chlorine and ammonia addition (dashed lines) and preformed chloramines (solid lines) at pH 6, 2 mg Cl_2/L, 4:1 Cl_2:N mass ratio, 150 µg/L Br^-, 3 mM total carbonate

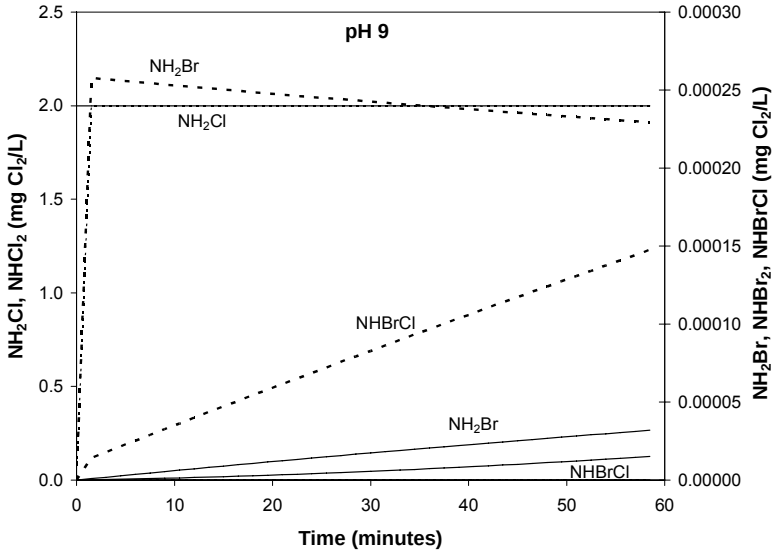


Figure 7-27 – Model predictions of haloamine formation from simultaneous chlorine and ammonia addition (dashed lines) and preformed chloramines (solid lines) at pH 9, 2 mg Cl_2/L, 4:1 Cl_2:N mass ratio, 150 µg/L Br^-, 3 mM total carbonate

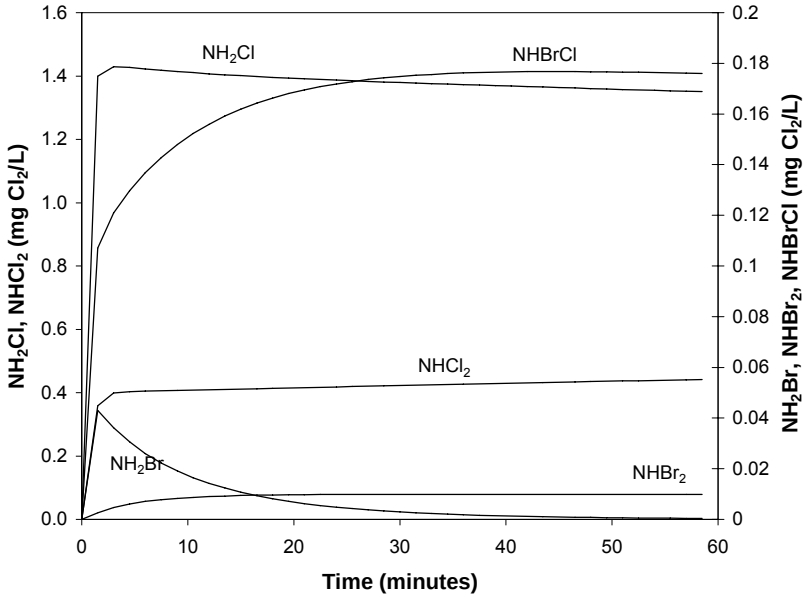


Figure 7-28 – Model predictions of haloamine formation from 10 second prechlorination prior to ammonia addition at pH 6, 2 mg Cl_2/L, 4:1 Cl_2:N mass ratio, 150 µg/L Br^-, 3 mM total carbonate

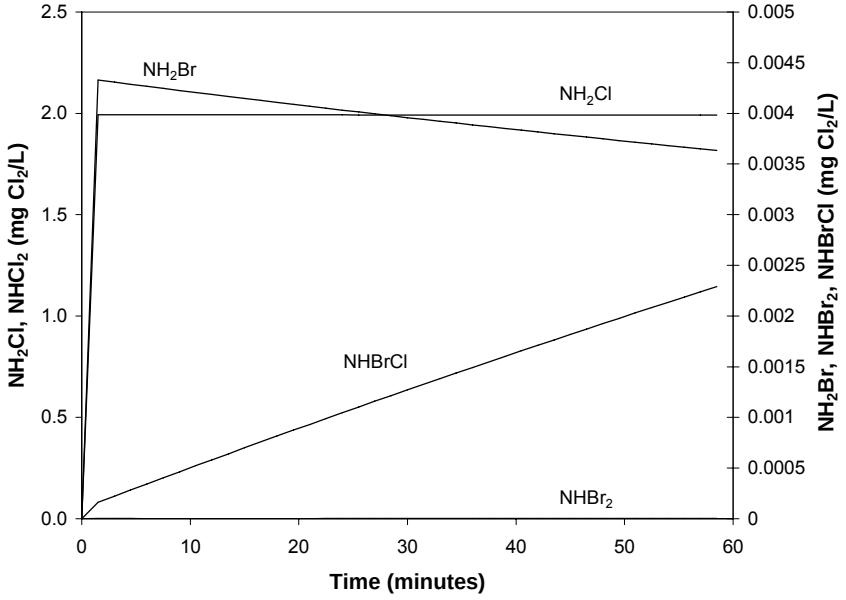


Figure 7-29 – Model predictions of haloamine formation from 10 second prechlorination prior to ammonia addition at pH 9, 2 mg Cl_2/L, 4:1 Cl_2:N mass ratio, 150 µg/L Br^-, 3 mM total carbonate

7.6. IMPLICATIONS FOR DXAA FORMATION

The concentration of the different haloamines that may be present in waters containing bromide is key to determining their influence on DBP formation. The significant impact of chemical addition (*i.e.* prechlorination, simultaneous addition of chlorine and ammonia, or preformed chloramines) on haloamine speciation illustrates the importance of understanding these reactions. Kinetic experiments with natural waters demonstrated that DXAA formation during chloramination is characterized by an initial rapid period of formation followed by a period of slower formation, and that the bromine-substituted species (BCAA and DBAA) formed more rapidly than DCAA. The pH also had a significant influence on DXAA formation. More rapid DXAA formation kinetics were observed at pH 7 than at pH 9. The initial rapid period of formation (*i.e.*, <30 minutes) was independent of pH; however, after 30 minutes, more rapid kinetics were observed at lower pH. These pH trends parallel the impact pH has on haloamine speciation. Monochloramine and monobromamine decay, as well as bromochloramine formation, is acid catalyzed. In addition, as pH decreases the free chlorine and bromine species are present in their more reactive forms. The bromine-substituted haloamines have been shown to be considerably more reactive and have much shorter half-lives than their chlorine-substituted counterparts. At low pH, the higher concentrations of the bromamines, bromochloramine, and dichloramine (which decomposes into HOCl) result in greater HAA formation, and because the bromine-substituted haloamines are very reactive and have short half-lives, they may react quickly with any NOM present, resulting in rapid bromine-substituted HAA formation kinetics. The absence of formation at later times (Figure 5-2) may be due to the absence of bromine-substituted haloamines in the water, not an absence of NOM reactivity toward them. A better understanding of haloamine speciation coupled with haloamine-NOM reactions will

allow the development of strategies to limit the formation of the more reactive haloamine species, thus limiting DBP formation.

CHAPTER 8: Conclusions and Recommendations

8.1. CONCLUSIONS

Chloramines are an attractive alternative to chlorine to limit DBP formation. However, significant concentrations of HAAs can still be formed. This study not only provides additional insight into the formation of HAAs during chloramination, but also the underlying haloamine chemistry responsible for their formation.

8.1.1. Impact of Natural Organic Matter on HAA Formation

NOM characteristics and concentration, and treatment processes that remove NOM, can have a significant effect on DXAA formation. NOM in the hydrophilic fraction was more reactive in forming DXAA during chloramination than the NOM in the hydrophobic fraction. The effectiveness of treatment on DXAA formation is largely related to overall DOC removal, although preferential removal of more reactive NOM fractions also may contribute to reduced DXAA formation. Reducing the organic precursor concentrations as much as possible is a strategy that may be effective in controlling DXAA formation. Both hydrophobic and hydrophilic NOM fractions should be removed, but preference should be given to the hydrophilics. Consequently, treatment processes that favor hydrophilic DOC removal, such as biological treatment, may need to be considered. On the other hand, treatment processes that remove DOC will increase the Br^-/DOC ratio, which will shift the DXAA speciation more toward the bromine-substituted species and in some cases may increase the DXAA yield.

8.1.2. Influence of pH, Cl_2/N Ratio, Temperature, and Bromide Concentration on DXAA Formation

ANOVA analyses of DXAA formation in natural waters over a broad variety of experimental conditions that reflected ranges found in treatment plants usually pointed to pH as being the most significant factor in DXAA formation. DXAA formation decreased as the pH increased. Therefore, utilities interested in decreasing DXAA formation should first examine the possibility of raising the pH of their water.

The impact of bromide can be viewed from several perspectives: the DXAA mass concentration or yield, DXAA molar concentration or yield, and DXAA speciation, which can be described by n_D'. Generally, bromide impacts the DXAA speciation and DXAA mass concentration or yield more so than DXAA molar concentration or yield. A shift in speciation to the bromine-substituted species occurred as the bromide concentration increased and the pH decreased. Because of the higher molecular weight of bromine in comparison to chlorine, the shift in speciation implies an increase in the DXAA mass yield or concentration. The overall results suggest that the DXAA molar yield generally will not increase over the range of Br^-/DOC ratios typical of practice. A source water experiencing a large increase in bromide concentration, however, may exhibit an increase in the DXAA molar yield. An increase in the Br^-/DOC ratio is undesirable from two perspectives. First, the regulations are based on mass concentration, so the likelihood of violating the HAA MCL increases. Second, the bromine-substituted HAAs may be of greater health concern.

ANOVA analyses indicated that the Cl_2/N mass ratio was the next most significant contributor to DXAA formation after pH and bromide. DXAA formation decreased as the Cl_2/N ratio decreased. Temperature and chloramine residual also impacted DXAA formation, but were much less influential than the aforementioned

factors. DXAA formation increased as the temperature increased, and the impact of temperature was more pronounced as the Cl_2/N ratio increased. Although reducted formation of DXAAs is expected for lower chloramine residuals, the amount of reduction was small in this research. Therefore, managing DXAA reduction by chloramine residuals should be used only as a last resort.

8.1.3. DXAA Formation Kinetics

The rate of DXAA formation during chloramination is a key consideration in determining strategies for minimizing formation. The kinetics of DXAA formation during chloramination are characterized by an initial rapid period of formation followed by a period of slower formation, and the bromine-substituted species (BCAA and DBAA) form more rapidly than DCAA. In Metedeconk River source water chloraminated at pH 8 and spiked with 0.5 mg/L Br^-, for example, DBAA formation was essentially complete, and 50% of the 72-hour BCAA had formed after 5 minutes, whereas DCAA continued to form for 72 hours. Only approximately 10% of the 72-hour DCAA concentration formed in the first 5 minutes of chloramination. The pH also had a significant influence on DXAA formation kinetics. More rapid DXAA formation kinetics occur as pH decreases. However, in batch kinetic studies, the initial rapid period of formation (i.e. <30 minutes) was independent of pH, but after 30 minutes, more rapid kinetics were observed at lower pH.

Many utilities have begun to use chloramines as a secondary disinfectant in response to current and anticipated DBP regulations; thus, many plants now have a significant period of free chlorination prior to ammonia addition for purposes of meeting CT requirements. During even short periods of prechlorination (5 or 20 minutes), significantly more DXAA formation, as well as formation of mono- and tri-halogenated acetic acids, occurred relative to chloramination alone. In addition, longer

prechlorination periods result in greater HAA formation. During the prechlorination period, free chlorine reacts with most of the fast-reactive NOM sites. As a result, after subsequent ammonia addition and chloramine formation very little additional DXAA is formed. Therefore, the general expectation is that very little of the DXAA formation in chlorination/chloramination plants is associated with the chloramination step, despite the dramatic difference in the chloramine and chlorine contact times that is typical of such plants. Thus, HAA control strategies should be focused on the chlorination step in plants that prechlorinate prior to chloramination. Many utilities now face a chlorine/chloramines/CT balancing act that will only get more difficult in the future. Therfore, utilities that may have difficulty meeting the HAA MCL should prechlorinate for the shortest time that still allows them to meet disinfection requirements.

8.1.4. Haloamine Reactivity

When bromide is present in source water, bromine-substituted haloacetic acids typically form during chloramination. Monochloramine is the dominant haloamine species under drinking water treatment conditions. In the presence of bromide, however, bromine-substituted haloamines, such as mono- and dibromamine, as well as bromochloramine may also form. The bromine-substituted haloamines monobromamine, dibromamine, and bromochloramine predominantly form DBAA (over 70% of the total HAA_9 formation on a molar basis), and are significantly more reactive than monochloramine in forming HAAs. In Lake Austin source water, each of the bromine-substituted species formed approximately 6 times the HAA concentration than monochloramine. Additionally, Metedeconk River source water was more reactive; monobromamine and dibromamine resulted in 7 and 12 times the HAA formation than from monochloramine, respectively. These data illustrate the importance of source water characteristics on the relative reactivity of each species. The greater reactivity of

Metedeconk River was expected based upon its higher SUVA (4.87) compared to Lake Austin (2.11). Therefore, the varying characteristics of NOM among source waters is a significant factor in determining NOM's reactivity with the different bromine- and chlorine-substituted haloamines that may form in the presence of bromide during chloramination. Even though bromine-substituted haloamines are present in much lower concentrations than monochloramine under drinking water treatment conditions, they are still reactive enough to play a role in HAA formation. Limiting the formation of bromine-substituted HAAs is of particular interest because they may pose a greater health risk than their chlorine-substituted counterparts.

8.1.5. Haloamine Formation and Speciation

The concentration of the different haloamines that may be present in waters containing bromide is key to determining their influence on DBP formation. The manner of chemical addition (*i.e.* prechlorination, simultaneous addition of chlorine and ammonia, or preformed chloramines) has a significant impact on haloamine speciation. When chlorine is present it may react with bromide to form HOBr or ammonia to form chloramines. Therefore, during prechlorination, elevated DBP formation occurs because free chlorine, as well as HOBr that forms from the oxidation of Br^-, is available to react with NOM. During simultaneous addition of chlorine and ammonia (or nearly so), even brief periods of free chlorine contact with Br^- and NOM result in greater formation of bromine-substituted haloamines, and therefore may result in greater DBP formation, than waters that experience minimal contact with free chlorine, such as those dosed with preformed chloramines. Additional studies to determine the impact of very brief periods of prechlorination on DBP formation are warranted to determine if utilities that treat high bromide source waters would benefit from disinfecting with preformed chloramines made in low bromide water instead of simultaneous addition of chlorine and ammonia.

During chloramination, HAA formation is directly related to the types and concentrations of haloamines that form. Factors that affect the stability of monochloramine also have a significant influence on haloamine speciation, and therefore on DXAA formation as well. For example, more rapid DXAA formation kinetics were observed at pH 7 than at pH 9, and the initial rapid period of formation (i.e. <30 minutes) was independent of pH; however, after 30 minutes, more rapid kinetics were observed at lower pH. These pH trends parallel the impact pH has on haloamine speciation. Monochloramine and monobromamine decay, as well as bromochloramine formation, is acid catalyzed. In addition, as pH decreases the free chlorine and bromine species are present in their more reactive forms. At low pH, higher concentrations of bromamines, bromochloramine, and dichloramine (which decomposes into HOCl) result in greater HAA formation.

During the prechlorination period, bromide present in the source water can be oxidized by free chlorine to form HOBr, and both it and HOCl can react NOM, forming DBPs. In addition, because HOCl reacts signifcantly more rapidly with Br^- to form HOBr than OCl^-, prechlorinating at pH values in which OCl^- is the dominant species, will result in less HOBr formation; and therefore, less bromine-substituted DBP formation.

The insight this research provides in terms of the detection and quantification of bromine-substituted haloamines was made possible by the use of membrane introduction mass spectrometry (MIMS), the value of which to the study of disinfection chemistry was proven by this research. MIMS can differentiate between the many different haloamine species that may be present during drinking water treatment, and in conjuction with spectophotometric techniques, can both differentiate and quantify the concentrations of the chloramines, bromamines, and bromochloramine. Previously, the differentiation among the individual haloamine species in concentrations typical of drinking water

treatment was not possible; only monochloramine, free chlorine, or total chlorine could be measured. Additionally, bromine-substituted haloamines are also measured as "total chlorine" and HOBr is measured as "free chlorine". In light of its value, further effort is warranted to improve this technique. Currently, detection limits for haloamine species are approximately 0.2 mg/L as Cl_2. Increasing the sensitivity of this technique in measuring the bromine-substituted haloamines would allow the further study of chloramine disinfection under conditions where bromine-substituted haloamines are present at very low concentrations, such as during preformed chloramination.

A unified haloamine kinetic model was developed to aid in understanding the complexity of haloamine chemistry. In addition to the ability to predict monochloramine formation and decay, this model also tracks the formation and decay of the bromine-substutited species that may form, such as HOBr, NH_2Br, $NHBr_2$, and NHBrCl. This model incorporated individual rate constants previously determined by other researchers into a unified model. Only the rate constants for NHBrCl formation and decay were calibrated with data obtained from the batch studies of this research. Excellent predictions of monchloramine formation and decay was achieved in experiments with preformed chloramines. Excellent predictions were also obtained between the measured and predicted monochloramine, bromochloramine and dibromamine concentrations at both pH 7.2 and 9 after 5 minutes of prechlorination. However, at the longer reaction times, the model tended to underpredict the NH_2Cl concentration and overpredict the NHBrCl concentration; this tendency is most obvious in the pH 7.2 results. The differences between the measured and predicted concentrations may be a result of discrepancies in the mechanism of bromochloramine decay. Therefore, the elucidation of the mechanism of bromochloramine decay may result in better model predictions.

Water treatment requires a balance between producing a water free of pathogens while limiting carcinogenic and mutagenic by-products that may form as a result of disinfection. A better understanding of haloamine speciation coupled with more knowledge of haloamine-NOM reactions will allow the development of strategies to limit the formation of the more reactive haloamine species, thus limiting DBP formation during chloramination.

8.2. RECOMMENDATIONS FOR FUTURE WORK

The results of this research suggest that additional work to further understand the complex mechanisms of haloamine formation and decay is needed. In particular, the incorporation of more robust reaction mechanisms describing the decay of dibromamine and chlorobromamine should enable the unified haloamine kinetic model developed in this research to make more accurate predictions of haloamine concentrations. In addition, it is thought that bromine-substituted haloamines may react with their chlorine-substituted counterparts to form bromochloramine. Therefore, further study is warranted to determine if such reactions are of significance, and if so, they should be incorporated into the model. Further effort is also needed to add haloamine reactions with NOM to the model allowing accurate predicts of DBP formation.

Optimization of MIMS to lower the detection limits, especially for the bromine-substituted haloamines, which are present in very low concentrations, is also needed. Several possibilities include further investigations of membrane materials, the incorporation of a jet separator, which would limit the amount of water introduced to the mass spectrometer, or the use of a direct insertion probe. These lower detection limits will allow further study of the influence of water quality and treatment conditions on haloamine speciation under conditions where they may be present in very low concentrations.

In addition to the further study of haloamine chemistry, a greater knowledge of bromine-substituted haloamine reactivity is also needed. This research focused on HAA formation; however, significant peaks other than those associated with HAAs were observed in the GC chromatograms obtained during the bromine-substituted haloamine reactivity experiments. The relative abundance of the unkown peaks in comparison with those of the HAAs warrants further investigation to identify these "unknown" DBPs.

Appendix – Analysis of Variance (ANOVA)

EXPERIMENTAL DESIGN

Analysis of variance (ANOVA) was used to identify the water quality and chloramination variables that were most important in DXAA formation. This screening approach used a fractional factorial experimental design (Table A-1) to systematically evaluate the many factors that may influence DXAA formation during chloramination (*i.e.*, Cl_2/N ratio, pH, temperature, chloramine residual concentration, and bromide concentration). Two levels (Table 3.1) of each of the five variables were selected for these experiments. A summary of the levels of each of the five experimental variables is provided in Table 3.2. The ANOVA highlights the relative significance and contribution of each evaluated factor to DXAA formation.

Table A–1 – Sixteen trial orthogonal array for assessing the influence of selected chloramination and water quality conditions on various waters and NOM fractions

Trial No.	Column Number*														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
2	1	1	1	1	1	1	1	2	2	2	2	2	2	2	2
3	1	1	1	2	2	2	2	1	1	1	1	2	2	2	2
4	1	1	1	2	2	2	2	2	2	2	2	1	1	1	1
5	1	2	2	1	1	2	2	1	1	2	2	1	1	2	2
6	1	2	2	1	1	2	2	2	2	1	1	2	2	1	1
7	1	2	2	2	2	1	1	1	1	2	2	2	2	1	1
8	1	2	2	2	2	1	1	2	2	1	1	1	1	2	2
9	2	1	2	1	2	1	2	1	2	2	2	2	1	2	1
10	2	1	2	1	2	1	2	2	1	2	1	2	1	2	1
11	2	1	2	2	1	2	1	1	2	1	2	2	1	2	1
12	2	1	2	2	1	2	1	2	1	2	1	1	2	1	2
13	2	2	1	1	2	2	1	1	2	2	1	1	2	2	1
14	2	2	1	1	2	2	1	2	1	1	2	2	1	1	2
15	2	2	1	2	1	1	2	1	2	2	1	2	1	1	2
16	2	2	1	2	1	1	2	2	1	1	2	1	2	2	1

*Parameter main effect column assignments: pH = 1; Cl_2/N = 3; Temperature = 4; Br^- Concentration = 8; and Chloramine Residual Concentration = 15. All two-factor interactions are assigned to remaining columns according to Taguchi (Ross, 1988).

The fractional factorial experimental design facilitated statistical assessment and comparison of the numerous factors that influence DXAA formation. A complete ANOVA table for all 192 experiments previously outlined (*i.e.*, 12 waters x 16 trials) is summarized in Table A–2. The key statistical results were found in the F-statistic and the percent contribution. The former determined the significance of a given parameter (at various levels of confidence), while the latter ranked the parameters according to their contribution to the variation in the DXAA formation data. All main effects (Cl_2/N ratio, pH, temperature, Br^- concentration, and chloramine residual) for each water type could be statistically evaluated. Moreover, each water type could be blocked so any desired combination of water type(s) could be statistically compared against other water type(s).

Table A–2– Summary ANOVA table for all 192 trials in the initial batch screening experiments

Parameters[a]	Degrees of Freedom	Sums of Squares	Mean Square	F-Statistic	Percent Contribution
Water Type	11				
Cl_2/N Ratio	1				
pH	1				
Temperature	1				
Chloramine Residual	1				
Br^- Concentration	1				
Cl_2/N x pH	1				
Cl_2/N x Temperature	1				
Cl_2/N x Residual	1				
C_2/N x Br^- Conc.	1				
pH x Temperature	1				
pH x Residual	1				
pH x Br^- Conc.	1				
Temperature x Residual	1				
Temperature x Br^- Conc.	1				
Residual x Br^- Conc.	1				
Total	26				**100**

[a] The list of parameters will be simplified by dropping all insignificant variables and especially two-factor interactions into an error term.

EXAMPLE CALCULATION

Notation (adapted from Ross (1988)):

- y = observation (DXAA concentration)
- y_i – i^{th} response (i = 1-16)
- N = total number of observations (16)
- T = sum of all observations (data points)
- A = factor under investigation
    - A_1 = sum of observations under1st level of factor
    - A_2 = sum of observations under 2nd level of factor
- SS_T = total sums of squares

- SS_A = variation due to factor A
- SS_e = variation due to error
- df = degrees of freedom
- MS_A = mean square of factor A
- F_A = F ratio
- SS'_A = expected sum of squares due to factor A

Relevant equations (adapted from Ross (1988)):

- $SS_T = \sum y_i^2 - \frac{T^2}{N}$
- $SS_A = \frac{(A_1 - A_2)^2}{N}$
- $SS_T = SS_A + SS_e$
- $df_T = df_A + df_e$
- $MS_A = \frac{SS_A}{df}$
- $F = \frac{MS_A}{MS_e}$
- $SS'_A = SS_A - SS_e * df_A$
- $PercentContribution = \frac{SS'_A}{SS_T}$

Table A–3 – Example ANOVA summary of various factors influencing the production of DXAA (μmol/L) in Lake Austin source water

Parameter	df	SS	MS	F	SS'	Percent Contribution (%)
pH	1	0.0211	0.0211	48.81***	0.0027	39.8
Cl_2/N ratio	1	0.0079	0.0079	18.21***	0.0075	14.3
Temperature	1	0.0018	0.0018	4.24*	0.0014	2.7
Bromide Level	1	0.0129	0.0129	29.76***	0.0125	23.9
Chloramine Residual	1	0.0039	0.0039	9.06**	0.0035	6.7
Error	10	0.0043	0.0004			12.5

Total percent contribution is equal to 100%
***: Significant at 99% Confidence
**: Significant at 95% Confidence
*: Significant at 90% Confidence
NS: Not Significant

Table A–4 – Example combined ANOVA summary of various factors influencing the production of DXAA (μmol/L) in Metedeconk River source, Lake Austin source and algal source waters

Parameter	df	SS	MS	F	SS'	Percent Contribution (%)
Water	2	0.023	0.011	18.96***	0.021	12.5
pH	1	0.062	0.062	104.42***	0.062	36.0
Cl_2/N ratio	1	0.013	0.013	22.57***	0.013	7.5
Temperature	1	0.010	0.010	16.26***	0.009	5.3
Bromide Level	1	0.026	0.026	43.85***	0.026	14.9
Chloramine Residual	1	0.007	0.007	11.74***	0.006	3.7
Error	40	0.024	0.001			19.9

Total percent contribution is equal to 100%
***: Significant at 99% Confidence
**: Significant at 95% Confidence
*: Significant at 90% Confidence
NS: Not Significant

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Vita

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